

# 4 General Methods of Extraction

## 4.0 INTRODUCTION

In an extraction process, a specific amount of energy is required to reduce or release a metal ion present in a compound (solid or liquid) in association with other elements and to collect the metal in its elemental form. During metal extraction, the bulk of the metal is separated from the impurities present in the ore by using a system which invariably comprises more than one phase. The metal enters the metallic phase while the impurities enter the nonmetallic phase or phases. The driving force for the reactions involved in metal extraction depends on the differences in the chemical potentials of the chemical elements. The significance of chemical potential gradients in an extraction process has been discussed in Chapter 2. To briefly recapitulate: during a chemical reaction, an element tends to move from a high to a low chemical potential state. In each extraction process, the basic aim is to create conditions conducive to such a transfer, which facilitates the extraction of a metal or its compound.

In metal extraction, a vast majority of metallurgical reactions are made to take place at elevated temperatures because then the ore compounds become relatively unstable, facilitating the release of the metal. This is the basis of *pyrometallurgy*. In *electrometallurgy*, the dissociation or decomposition of a compound in solution (i.e., reduction of an ion) is brought about by employing electrical forces. In *hydrometallurgy*, the reduction process depends on the judicious manipulation of the chemical reactions taking place in an aqueous solution.

## 4.1 PYROMETALLURGY

Despite the rapid developments in hydrometallurgy and electrometallurgy over the last hundred years, pyrometallurgy still remains the principal means of metal extraction, both in the number of applications and in the tonnage of metal produced. Pyrometallurgy deals with the methods of extraction of metals from their ores and their refining, and is based on chemical and physical changes occurring at high temperatures, i.e., 500–2000°C.

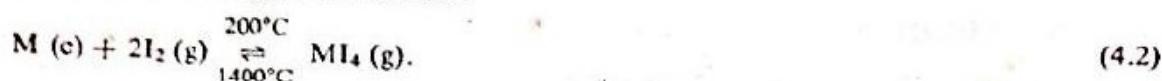
A high-temperature process is often cheaper and more versatile than other competing methods such as electrometallurgy and hydrometallurgy because of the reasons now given.

At a high temperature, the reaction rate is accelerated. A rapid reaction rate leads to the increased production of a metal (for a given size of reactor). Further, a high-temperature process permits the use of inexpensive reducing agents or raw materials that are cheaper than those required for a low-temperature process. It should be noted that the rate of most reactions is approximately doubled for every 10°C rise in temperature, and the higher the temperature, the smaller the activation energy barrier that opposes the progress of the chemical reaction.

Pyrometallurgical extraction takes advantage of the ability to shift the reaction equilibrium with temperature. For example, at 25°C, the equilibrium position of the reaction



is far to the left, but, at 1200°C, it shifts far to the right. In other words, carbon cannot reduce  $ZnO$  except at elevated temperatures, i.e., at a minimum of 900°C for continuous reduction at 1 atm. Another example that illustrates the effect of temperature on the reaction equilibrium is the iodide refining process for refractory metals such as titanium and zirconium. When a crude metal  $M$  is made to react with iodine at a low temperature (the reaction equilibrium being shifted to the right), metallic iodide vapour is formed. This vapour is transported to a hot zone (the reaction equilibrium being shifted to the left), where it decomposes into the pure metal and regenerates iodine according to the reaction



The physical separation of a product metal from waste is facilitated when the products are liquefied or vaporized at high temperatures. Further, at these temperatures, the liquid metal and liquid slag that are formed separate out, facilitating metal extraction. Some of the common metals such as iron, lead, zinc, copper, aluminium, magnesium, sodium, and antimony are produced by a process where the metal is reduced to either the liquid or the gaseous state, permitting its separation from the residue. One of the reasons why refractory metals such as titanium, zirconium, molybdenum, tantalum, and niobium are very expensive is that they are reduced directly to the solid metal. This requires an expensive process either to separate the metal from the residue or to pre-purify the metal compound so that no residue remains after reduction.

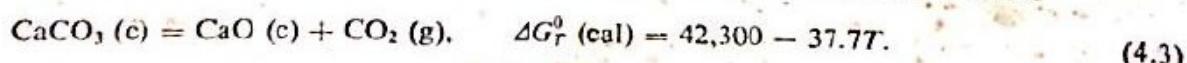
Pyrometallurgy can bring about the reduction of a compound, which cannot take place in the presence of water. This advantage stems from its ability to extract the reactive metals which cannot be reduced from an aqueous solution. Consequently, only pyrometallurgy or fused salt electrolysis can be used to extract the highly reactive metals, namely, the alkaline earth metals, zirconium, and titanium.

A high-temperature process has the inherent ability to treat large tonnages of ores in a compact space, which leads to a saving in the capital cost. Even a small electric furnace, by using a power input of a very high order, can achieve a very high production rate. This, however, is not true of an electrometallurgical process, either at the room temperature or at a high temperature, because the voltage value chosen for the process must necessarily be low, depending on the decomposition voltage of the compound to be electrolyzed. Moreover, there is always a limiting current density.

We now discuss the three main steps employed in pyrometallurgy, namely, calcination, roasting, and smelting.

#### 4.2 CALCINATION

*Calcination* is the thermal treatment of an ore that brings about its decomposition and eliminates the volatile product—usually carbon dioxide or water. The temperature required for calcination can be calculated from the free energy-temperature relationship for the reaction under consideration. For example, the reaction for the decomposition of calcium carbonate in a kiln is



When the  $CO_2$  pressure is 1 atm,  $\Delta G_f^0$  becomes equal to 0 and  $T$  becomes equal to 1123 K or 850°C, so that a kiln temperature of 1000°C would be sufficient to provide a rapid temperature rise in the mineral particles and to reach the decomposition temperature. Since the reaction is

endothermic, the rate of decomposition is probably controlled by the rate of heat transfer into the particle. As a result, even higher kiln temperatures can be expected so as to increase the production rate, but at some cost in fuel. Since the solid residual product is likely to be porous in texture and permeable, the gaseous product can easily escape. Further, the pressure at the decomposition front is likely to be a little higher than the atmospheric pressure.

The decomposition temperature of a carbonate is the temperature at which the partial pressure of  $\text{CO}_2$  ( $p_{\text{CO}_2}$ ) equals 1 atm. It is obvious that most carbonates actually *start* to decompose at temperatures lower than the decomposition temperature of calcium carbonate (e.g.,  $\text{MgCO}_3$  at  $417^\circ\text{C}$ ,  $\text{MnCO}_3$  at  $377^\circ\text{C}$ , and  $\text{FeCO}_3$  at about  $400^\circ\text{C}$ ). This fact can be used for differential calcination. For example, a magnesium ore that contains both magnesium carbonate and calcium carbonate can be beneficiated by calcining the ore around the decomposition temperature of  $\text{MgCO}_3$ . Water is used to leach out the resulting  $\text{MgO}$ , and the undecomposed  $\text{CaCO}_3$  is left behind.

#### 4.3 ROASTING

The *roasting* of an ore or a concentrate is a process which precedes smelting in pyrometallurgy and leaching in hydrometallurgy. In general, very few ores and concentrates in their native form are suitable for direct conversion to the metal. An oxide is more easily reduced to the metal than a sulphide, and leaching becomes easier if the metal were present as a sulphate, chloride, or oxide. Therefore, the mineral constituent of an ore must be converted into another chemical form. Such a conversion can be brought about by roasting. The main purpose of calcination is to decompose an ore, whereas roasting, by employing oxygen or some other element, aims at the chemical conversion of an ore. Traditionally, roasting was chiefly used to remove sulphur or other elements such as arsenic and tellurium in the form of a volatile oxide from an ore. Nowadays, however, roasting encompasses a wide variety of operations including reduction, sulphation, and chloridization, wherein the ore is heated to a temperature below the fusion point of its constituents. The product thus obtained becomes amenable to subsequent treatment for the extraction of the metal.

We now discuss some typical roasting operations to emphasize the importance of roasting in metal extraction processes.

#### OXIDIZING ROASTING

*Oxidizing roasting*, which is the most important roasting process, burns out the sulphur from a sulphide ore and replaces it, in whole or in part, by an oxide. The general reaction is



For example, in the case of zinc sulphide, the reaction is



Reaction (4.5), however, gives only an overall picture of roasting. In reality, a complicated series of reversible reactions occur. During roasting, metal sulphates may also be formed. A high temperature is required to break up the sulphates, especially zinc sulphate.

When a sulphide ore is roasted to a point where almost the entire sulphur content is eliminated, the residue is called *dead roast*.

A catalytic agent often speeds up the roasting process. Quartz and other gangue materials often act as catalysts during roasting.

Roasting essentially depends on factors such as time (i.e., duration), temperature, the availability of oxygen or air, the physical condition of the ore, and the nature of the mechanical devices used. The durations of roasting processes vary greatly. For example, blast roasting is done in a mere flash of time, whereas hearth roasting takes hours, heap roasting months, and weather roasting years.

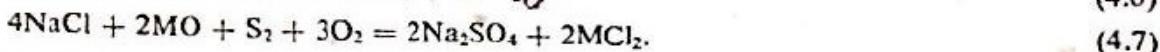
### VOLATILIZING ROASTING

*Volatilizing roasting* eliminates volatile oxides such as  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{ZnO}$  from an ore. In volatilizing roasting, the inflow of oxygen should be carefully controlled, as excessive oxidation may lead to the formation of non-volatile higher oxides.

### CHLORIDIZING ROASTING

*Chloridizing roasting* is carried out to convert certain metal compounds to chlorides under oxidizing or reducing conditions. Many metals, for example, uranium, beryllium, niobium, zirconium, and titanium, are extracted from their chlorides.

Some chloridizing reactions are



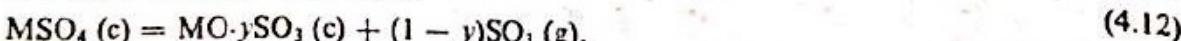
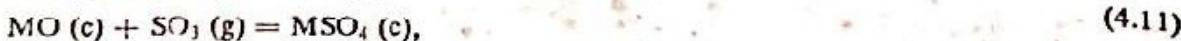
Reaction (4.6) is particularly suited to the roasting of a sulphide ore, which may be highly exothermic. For an oxide ore, reaction (4.7) is facilitated by the addition of elemental sulphur. Reaction (4.7) also represents the chlorination of a carbonate which decomposes on heating, giving an oxide. Sulphates and silicates may react with a chloride by a direct interchange of the elements and radicals without the addition of sulphur.

### OTHER KINDS OF ROASTING

Apart from oxidizing roasting, volatilizing roasting, and chloridizing roasting, there are other kinds of roasting processes, some of which are now mentioned. *Sulphating roasting* converts certain sulphide ores to sulphates, usually prior to leaching. An example of *magnetic roasting* is the controlled reduction of hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ). *Reduction roasting* is the partial reduction of an oxide ore prior to actual reduction smelting. *Blast roasting* or *sinter roasting* not only modifies the physical condition of an ore (e.g., agglomeration) but also helps in its partial oxidation.

### CHEMISTRY OF ROASTING

A large number of reactions are theoretically possible when a sulphide is roasted. Consider a sulphide  $\text{MS}$ , where  $\text{M}$  is a divalent metal. Some of the possible reactions are



[Examples of  $MO \cdot ySO_3$  are  $PbSO_4 \cdot PbO$  ( $y = \frac{1}{2}$ ),  $PbSO_4 \cdot 2PbO$  ( $y = \frac{1}{3}$ ), . . . .] At the temperatures commonly used for roasting, reactions (4.9) and (4.10) generally have large negative free energy changes and the  $SO_2/O_2$  equilibrium is far to the right. For example, in the case of  $FeS$ , the standard free energy change for reaction (4.10) is given by

$$\Delta G^\circ (\text{cal}) = -113,000 + 9.5T \log T - 1.965(10^{-3}T^2) - 6.7T.$$

At 1100 K, the equilibrium constant  $K$  for this reaction is calculated as  $1.2 \times 10^{18}$ . Therefore, the sulphide is converted to an oxide for a relatively small value of the partial pressure of oxygen ( $p_{O_2}$ ). Similarly, at 1100 K, the equilibrium constant for reaction (4.9) is calculated as  $2.76 \times 10^{13}$ . This value shows that at a temperature as high as 1100 K,  $SO_2$  is a stable phase, even in the presence of small amounts of oxygen. On the other hand, reactions (4.11)–(4.14) are such that both the temperature and the partial pressure of  $SO_2$  ( $p_{SO_2}$ ) determine which of the phases are stable. By using the phase rule, we can show that the system is univariant for the existence of a gas and for a mixture of two solid phases such as  $MSO_4 \cdot MO$ ,  $MSO_4 \cdot MO \cdot ySO_3$ , or  $MO \cdot MO \cdot ySO_3$ . In other words, two solids can coexist, at any given temperature, over a range of partial pressures of  $SO_2$ . However, were the gas phase, i.e.,  $SO_2$ ,  $O_2$ , or  $SO_3$ , in equilibrium with all the three solids, namely,  $MO$ ,  $MSO_4$ , and  $MO \cdot ySO_3$ , then the system becomes nonvariant, that is, equilibrium can be attained only at a point where both temperature and  $p_{SO_2}$  are defined.

#### 4.4 PREDOMINANCE AREA DIAGRAMS

The temperature at which roasting is carried out is an important factor in determining the nature of the product obtained. In order to get a desired product, we can determine the best operating temperature by knowing both the composition of the gas used in an industrial roaster and the equilibrium relationship in an M-S-O system. The isothermal behaviour of some M-S-O systems with respect to their relative stabilities can be represented by predominance area diagrams. These diagrams indicate, for a specified temperature, those solids which are in equilibrium with a gas having specified partial pressures of oxygen and sulphur dioxide. Thus, these diagrams serve to predict the type of solid present that would be in equilibrium with a roaster gas of a known composition. Even in the case of partial roasting, where equilibrium conditions do not prevail, these diagrams can be used to identify the type of the product formed as the reaction proceeds towards equilibrium. The high values of the equilibrium constants of reactions (4.9) and (4.10), as calculated, suggest that  $SO_2$  is always formed as soon as oxygen reacts with a sulphide, so that the concentration of  $SO_2$  must be taken into account.

The basis for drawing predominance area diagrams can be illustrated by taking Ni-S-O as an example (see Fig. 4.1a). At 1000 K, in this system, the condensed phase is made up of  $Ni$ ,  $NiO$ ,  $Ni_3S_2$ , and  $NiSO_4$ . The gas phase normally contains  $SO_2$  and  $O_2$ , but some  $SO_3$  and  $S_2$  may also be present, as indicated by reactions (4.9) and (4.11). At a specified temperature, the phase relation between any two condensed phases can be represented by a two-dimensional diagram in which the partial pressures of any two of the gaseous components are taken as the coordinates. In Fig. 4.1a,  $\log p_{SO_2}$  and  $\log p_{O_2}$  are chosen as the coordinates. Thus, the reaction between the condensed phases  $NiS$  and  $NiO$ , and the gases  $SO_2$  and  $O_2$  is represented by

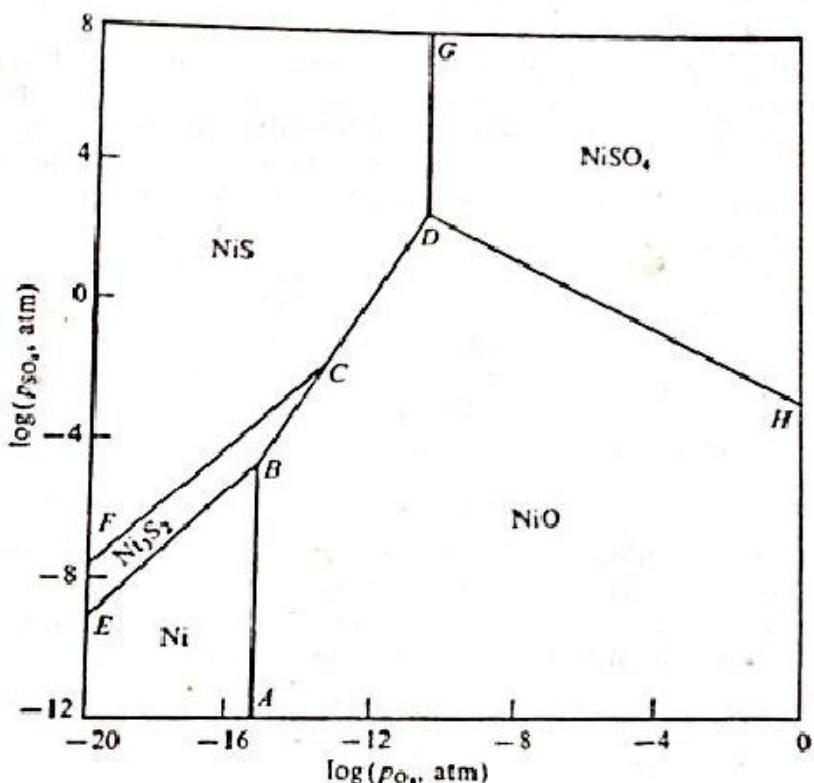


for which the equilibrium constant  $K'$  is given by

$$K' = \frac{p_{SO_2}}{p_{O_2}^{1/2}}$$

and

$\log p_{SO_4} = \frac{3}{2} \log p_{O_2} + \log K'$   
 $K'$  can be calculated by knowing the free energy change for reaction (4.15). In Fig. 4.1a,  $CD$



(a) Ni-S-O system at 1000 K

Fig. 4.1 Predominance Area Diagrams (after Kellogg and Basu, 1960) (cont.).

corresponds to reaction (4.15) and  $BC$  represents the equilibrium of the reaction



The corresponding equilibrium constant  $K'$  is given by

$$K' = \frac{P_{SO_2}^2}{P_{O_2}^{7/2}}$$

and

$$\log p_{SO_4} = \frac{3}{2} \log p_{O_2} + \frac{1}{2} \log K'.$$

It should be noted that the slope of  $BC$  is slightly different from that of  $CD$ .  $AB$  (in Fig. 4.1a) represents the equilibrium of the reaction



The corresponding equilibrium constant  $K'''$  is given by

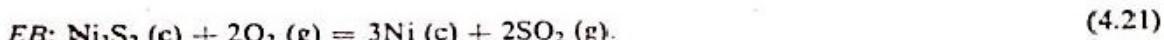
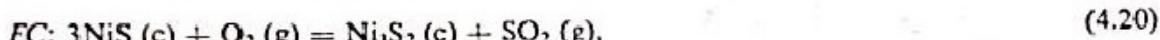
$$K''' = \frac{1}{p_{O_2}^{1/2}}$$

and

$$\log p_{O_2} = -2 \log K'''.$$

Obviously, the two phases Ni and NiO can coexist only at a fixed value of  $p_{O_2}$ . The equilibrium corresponding to reaction (4.17) is independent of  $p_{SO_2}$ .

Other lines in Fig. 4.1a represent the equilibria for the following reactions:



*FC* and *EB* are parallel to each other, each inclined at an angle of  $45^\circ$  to both the *x*- and *y*-axis. Thus, the stable portion of each bivariant equilibrium can be demarcated if the equilibrium constants for the various reactions are known.

The areas in Fig. 4.1a correspond to the predominance area for a particular condensed phase, both  $p_{SO_2}$  and  $p_{O_2}$  can be varied, and the system has two degrees of freedom. Along the lines, the system has one degree of freedom. The system is nonvariant when three condensed phases are present, as at the points *B*, *C*, and *D*.

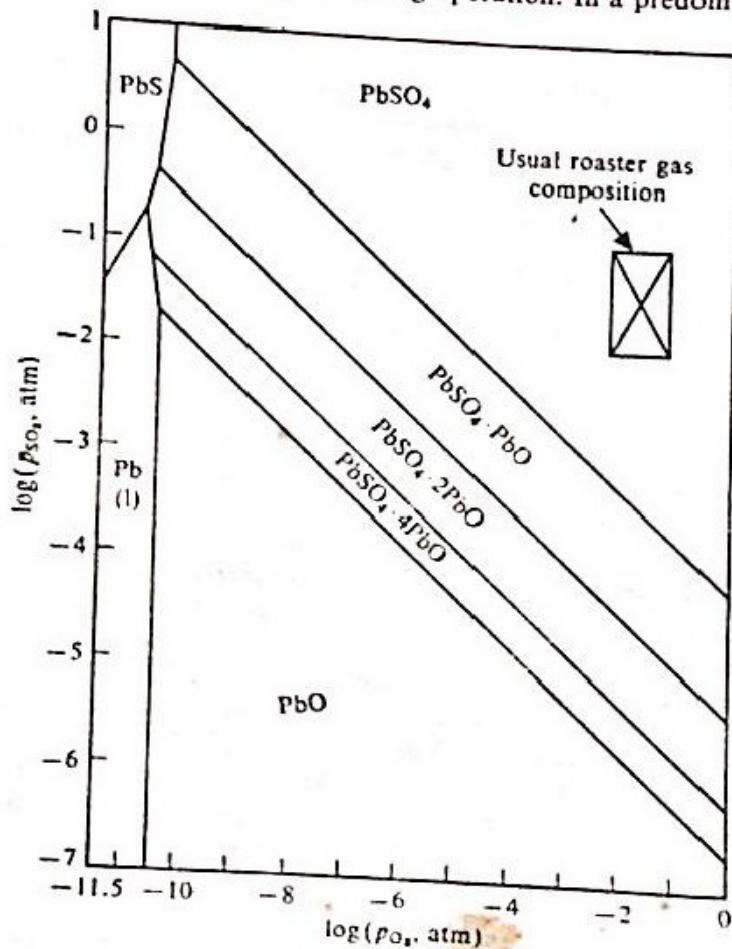
Predominance area diagrams, which are plotted from available thermodynamic data, provide data that help control roasting conditions so that the desired end products can be obtained. At 1000 K, if the roaster gas phase contains 10 per cent  $SO_2$  and 10 per cent  $O_2$ , it is evident from the predominance area diagram that  $NiSO_4$  is the thermodynamically stable phase. On the other hand, if the gas phase contains only 1 per cent  $SO_2$  and 1 per cent  $O_2$ , the final product is  $NiO$ . Nickel sulphate is formed under oxidizing conditions at a high partial pressure of  $SO_2$ . Although  $NiS$  can, in principle, be directly converted to  $NiSO_4$  at a high partial pressure of  $SO_2$ , in practice, it is more convenient to do so through the intermediate formation of  $Ni_3S_2$  and  $NiO$ .

If a given metal forms several oxides apart from the simple oxide mentioned and also sulphides, basic sulphates, and sulphates, additional equations have to be written, and the lines corresponding to them can be incorporated in Fig. 4.1a. For example, in the Pb-S-O system (see Fig. 4.1b),  $PbO$  can form several basic sulphates, namely,  $PbSO_4 \cdot 4PbO$ ,  $PbSO_4 \cdot 2PbO$ , and  $PbSO_4 \cdot PbO$  before it is converted to  $PbSO_4$ . Figure 4.1b illustrates various factors that govern roasting of lead sulphide. This figure also gives the composition of the roaster gas in a conventional roaster operating at  $827^\circ C$  and shows that the stable product obtained by roasting  $PbS$  should be  $PbSO_4$ . Since the  $PbS$  and  $PbO$  fields do not have a common boundary,  $PbO$  cannot be produced by roasting  $PbS$  in oxygen without some  $PbSO_4$  also being formed. This accounts for the difficulty encountered in dead roasting to  $PbO$  at  $827^\circ C$ . On the other hand, a sulphatizing roasting of  $PbS$  to yield  $PbSO_4$  can be carried out, but it is not desirable, as  $PbSO_4$  is insoluble in water. Figure 4.1b explains why  $PbSO_4$  is predominant in lead fumes rather than  $PbO$ . The possibility of a roast reduction reaction in which lead sulphide is converted to metallic lead by controlling  $p_{SO_2}$  and  $p_{O_2}$  is also

indicated in Fig. 4.1b. The reaction is



By studying the predominance area diagrams drawn for different temperatures, we can select the most suitable temperature for a given roasting operation. In a predominance area diagram,



(b) Pb-S-O system at 1100 K

Fig. 4.1 Predominance Area Diagrams (after Kellogg and Basu, 1960).

at a given temperature, the predominance areas for a given compound may have different locations for different metals. In the case of a mixed sulphide such as Fe-Cu sulphide, the roasting conditions can be predicted for the selective oxidation of Fe to an oxide ( $\text{Fe}_2\text{O}_3$ ) while retaining Cu as a sulphide.

Predominance area diagrams serve as a useful guide to the extraction of metals from sulphides. Moreover, by using predominance area diagrams, we can show that it would be more convenient to extract copper directly from the sulphide phase than from the oxide phase (see Chapter 7 for details). These diagrams also serve as a guide to the selective sulphation of minerals. For

example, the low stability of iron sulphates generally allows the selective sulphation of the other metals from sulphide mineral mixtures. Thus, copper ferrite can be converted to  $\text{CuSO}_4$  and  $\text{Fe}_2\text{O}_3$  by treating it with a mixture of  $\text{SO}_2$  and  $\text{O}_2$  in the range 600–800°C.

The foregoing discussion is based on the assumption that equilibrium conditions prevail. If a roasting operation is carried out under nonequilibrium conditions as is usually done in industrial processes, the nature of the solid phases formed in the roast are determined by the rates of the various reactions and by the mechanisms by which they proceed. These roasting reactions can often be catalyzed and, therefore, equilibrium is approached more easily. For example,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  intensify the decomposition rate of  $\text{MgSO}_4$ , while  $\text{SiO}_2$  has no effect on it. The addition of  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ , or  $\text{Mn}_2\text{O}_4$  also catalyzes the formation of  $\text{CoSO}_4$  and  $\text{ZnSO}_4$  (Skeaf and Espelund, 1973).

#### 4.5 ROASTING PRACTICE

As roasting is usually a preliminary step in many extraction processes, it is necessary to choose a roasting method that would facilitate subsequent operations. There is a wide variation in the requirements and conditions for the subsequent steps. Generally, a roasting process is chosen based on two major criteria, namely, the required physical condition and the required chemical composition of the product.

##### REQUIRED PHYSICAL CONDITION OF PRODUCT

If an ore is to be smelted in a blast furnace, the product should be coarse and cellular. For a reverberatory furnace or for a retort, the product should be fine. For leaching, the product should be porous in nature and the formation of insoluble compounds should be avoided.

##### REQUIRED CHEMICAL COMPOSITION OF PRODUCT

If lead is the prime metal to be recovered from a sulphide ore, it is desirable to eliminate almost the entire sulphur content before subsequent blast furnace smelting. For copper, the entire sulphur content need not be eliminated. In fact, a sufficient quantity of sulphur should be retained so as to produce a matte, which is mainly a mixture of iron sulphides and copper sulphides of a desired grade. For zinc, as for lead, almost the entire sulphur content should be eliminated. However, the formation of zinc ferrite should be avoided when zinc is extracted by leaching because it is difficult to leach the ferrite.

There are several other factors to be considered besides those mentioned. For example, the chemical composition of an ore and of the minerals present in it may or may not favour a particular roasting process. In the manufacture of sulphuric acid from sulphurous gases that are evolved during roasting, the actual roasting process must ensure the availability of a gas rich in  $\text{SO}_2$ , for example, fluidized bed roasting. If there are precious metals or other valuable recoverable metals which may be lost at excessively high temperatures, then we must adopt a low-temperature operation.

The most desirable combination of roasting operations is one that is commercially the most satisfactory in the long run. For example, a furnace gas containing  $\text{SO}_2$  and  $\text{SO}_3$  may be allowed to escape into the atmosphere or may be utilized in the manufacture of sulphuric acid. The utilization of sulphurous gases is recommended not only because it results in economic gain but also because it prevents atmospheric pollution. In most countries, there is strict legislation against atmospheric pollution by industrial waste gases.

### INDUSTRIAL ROASTING UNITS

The most widely accepted metallurgical roaster was first designed by MacDougall in England towards the end of the nineteenth century. It subsequently underwent many improvements but retained the basic principle of countercurrent flow of the solid ore and the oxidizing gases.

### MULTIPLE HEARTH ROASTING

A typical MacDougall type roaster (see Fig. 4.2) consists of several (about 10) circular brick hearths superimposed on each other. The entire structure is enclosed in a cylindrical brick-lined steel shell. Revolving mechanical rabbles attached to arms move over the surface of each hearth to continuously shift the ore. The arms are attached to a rotating central shaft that passes through

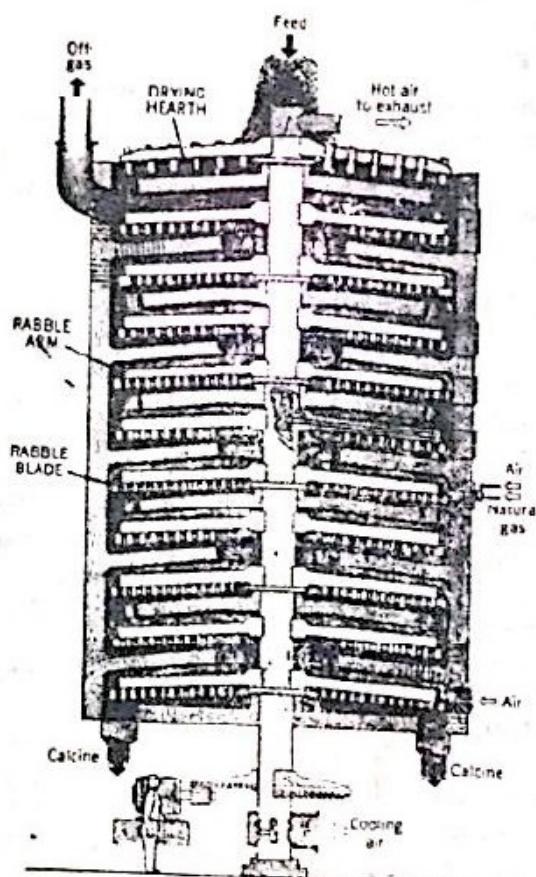


Fig. 4.2 MacDougall Type Hearth Roaster.

the centre of the roaster. The ore that is automatically discharged at the top hearth gradually moves downwards through alternate passages around the shaft and the periphery and finally emerges at the bottom. The oxidizing gases flow upwards, i.e., countercurrent to the descending charge. In a well-insulated roaster, external heating is unnecessary except when the charge is highly moist. The hearths at the top of the roaster dry and heat the charge. Ignition and oxidation of the charge occur lower down. In a MacDougall type roaster, although the roasting process can be effectively controlled, this roaster suffers from certain drawbacks, i.e., the roasting process

across the bed is equal to the weight of the particles per unit area of the bed. The particles now remain individually suspended and offer less resistance to the gas flow.

#### Stage 4

An even further increase in the gas velocity leads to the continued expansion of the bed. Since such an expansion results in an increase in the interparticle distance, the pressure drop across the bed continues to decrease as the gas velocity increases.

#### Stage 5

Finally, a stage is reached when the expansion of the bed becomes independent of the gas velocity. A major portion of the outgoing gas stream appears in the form of bubbles bursting on the surface of the bed which looks like a well-stirred boiling liquid. In this condition, the bed is said to be 'fluidized'. This fluidized bed, which has an apparent density distinctly different from the density of the solid, is capable of flowing like a liquid.

It is relatively easy to maintain the bed at a uniform temperature because of the high degree of mixing of the solids. This advantage together with the facility of handling both the solid feed and the product as pseudo-fluids has resulted in the widespread use of fluidized bed reactors, especially for highly exothermic or endothermic reactions. The thermal conductivities of some fluidized beds are known to be a hundred times higher than the thermal conductivity of the best metallic conductor, namely, silver.

The gas velocity required to fluidize a given bed can be determined by visual observation wherever possible, for instance, in a low-temperature glass model. For an actual reactor, however, the state of fluidization is ascertained by measuring the pressure drop across the bed. The fluidization behaviour of a bed can be graphically represented by plotting the pressure drop against the linear velocity of a gas passing through the bed (or the volume flow rate of a gas for a reactor that has a uniform cross-section). A typical fluidization curve is shown in Fig. 4.5. In

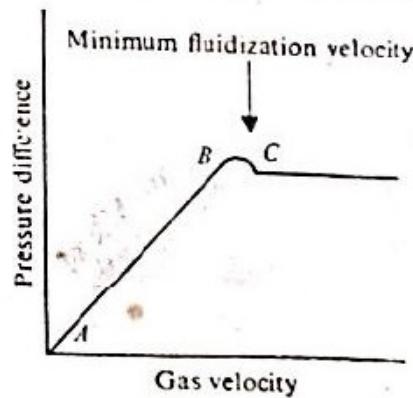


Fig. 4.5 Typical Fluidization Curve.

In this figure,  $AB$  represents the pressure drop for the stationary bed, i.e., before fluidization occurs. As the pressure drop across the bed approaches the lifting points, the bed is rearranged to provide minimum resistance to the gas flow, as indicated by the segment  $BC$ . Point  $C$  corresponds to both the maximum voidage of the packed bed (or the voidage corresponding to minimum fluidization) and the minimum gas velocity required for fluidization. Beyond  $C$ , the pressure drop becomes independent of the gas velocity. The minimum fluidization velocity is one of the most important

factors that govern the design of a fluidized bed. Although this velocity can be theoretically calculated, its value obtained from an experimental observation of the pressure drop is considered more reliable.

#### Ignition Temperature and Autogenous Roasting

From the foregoing discussion, it should be obvious that fluidized bed roasting is ideal for sulphide ores because the oxidizing reactions that take place during their roasting are highly exothermic. For any exothermic reaction of this kind encountered in roasting, there is a minimum temperature above which the reaction is sustained by the heat liberated by itself. In other words, when an ore particle is initially maintained at this minimum temperature in a stream of air and the roasting initiated by an ignition device, then the reaction continues to proceed even in the absence of any external heat. Such a reaction is termed *autogenous*.

In a fluidized bed roaster, the minimum temperature (or the ignition temperature) required depends on the characteristics of the ore as well as the conditions of ignition (geometry of a reactor and fluid flow). The ignition temperatures of some sulphide minerals, as determined under standardized conditions, are listed in Table 4.1. (The values are for oxidation in air, unless other-

Table 4.1 Ignition Temperature of Sulphide Minerals (°C)  
(after Dwight, 1945)\*

Mineral (%)	Formula	Size of grain (mm)		
		1	1-2	2
Pyrite	FeS <sub>2</sub>	325	405	472
Pyrrhotite	Fe <sub>3</sub> S <sub>6</sub> -Fe <sub>16</sub> S <sub>17</sub>	430	525	590
	FeS		535	
Ni, 73.5; S, 26.7		700	802	886
Co, 66.37; S, 33.63		574	684	859
Co, 70.20; S, 29.80		514	751	60.9
Stibnite	Sb <sub>2</sub> S <sub>3</sub>	290		340
Molybdenite	MoS <sub>2</sub>	240		308
Cinnabar	HgS	338		420
Chalcocite	Cu <sub>2</sub> S	430		679
Bi, 83.3; S, 16.7		500		627
Mn, 61.01; S, 33.98; Fe, 2.02		355		700
Argentite	Ag <sub>2</sub> S	605		875
Galena (in oxygen)	PbS	554		847
Millerite	NiS	573		616

\*See also Volsky, A. and Sergievskaya, E., Theory of Metallurgical Processes, trans. by I.V. Savin, Mir Publishers, Moscow (1971), Chapter 10.

is slow and the sulphurous gases evolved when a sulphide is roasted are unsuitable for the production of sulphuric acid because they do not contain sufficient  $\text{SO}_2$  and  $\text{SO}_3$ .

We now discuss some recently developed roasting techniques, namely, flash roasting and fluosolid roasting or fluidized bed roasting.

### FLASH ROASTING

In *flash roasting*, preheated ore particles are made to fall through a body of hot air, resulting in the almost instantaneous oxidation or 'flashing' of the combustible constituents of the ore, mainly sulphur. Initially, a flash roaster was constructed by merely removing intermediate hearths in a MacDougall type reactor and creating a large combustible zone. At present, however, a flash roaster is specially designed to ensure a large combustion zone. One such design is shown in Fig. 4.3.

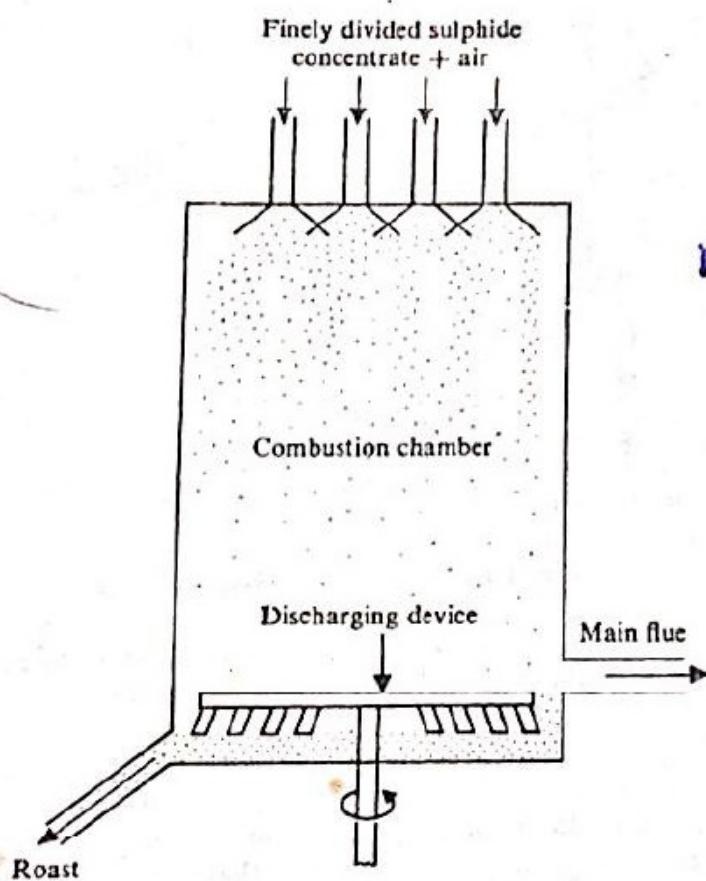


Fig. 4.3 Flash Roaster.

### FLUOSOLID ROASTING (FLUIDIZED BED ROASTING)

In *fluosolid roasting*, the ore particles are roasted while suspended in an upward stream of gas, as shown in Fig. 4.4.

When a gas is passed upwards through a bed of solid particles—small and preferably regular in size over the range 0.005–0.05 cm in diameter—the behaviour of the bed depends on the velocity of the gas.

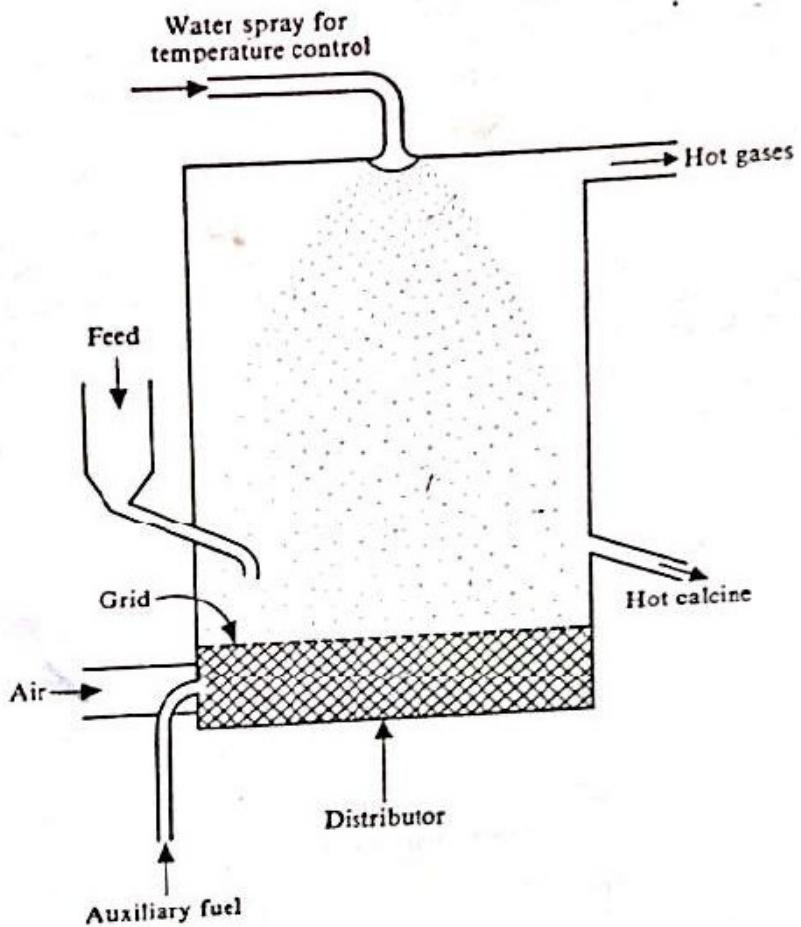


Fig. 4.4 Fluidized Bed Roaster.

We now describe certain distinct stages that are usually observed in the case of a porous bed that rests on a perforated grate through which a gas is forced upwards.

#### Stage 1

When the gas flow rate is very low, and since the bed is porous, the gas permeates the bed without disturbing the ore particles. In this stage, the pressure drop across the bed is proportional to the flow rate. Apart from the flow rate, the other factors that influence the pressure drop are the void fraction, the particle size, and the particle shape factor. (The particle shape factor is defined as the surface area of a sphere of equivalent volume divided by the actual surface area.)

#### Stage 2

As the gas velocity increases, the bed expands upwards due to the effect of the drag forces exerted by the gas stream. In this stage, the pressure drop across the bed depends on the gas velocity.

#### Stage 3

When the gas velocity is further increased, a stage is eventually reached when the pressure drop

wise mentioned.) Since the ignition temperature is the minimum temperature at which a mineral particle oxidizes fast enough to maintain or increase the temperature of the roaster, the ignition temperature values roughly indicate the temperature required for fluidized bed roasting.

A fluidized bed roaster has a high energy efficiency because it can be autogenously operated. Further, it is useful in the recovery of sulphur because the gas that it produces has a high  $\text{SO}_2$  content.

### SINTER ROASTING (BLAST ROASTING)

It should be noted that fine ores and concentrates have to be agglomerated before they can be charged into a blast furnace, otherwise heavy dust losses result. Sinter roasting is the treatment of a sulphide ore in a sintering machine where roasting and agglomeration take place simultaneously. (This is the standard practice for lead sulphide ores, in which case, the fine flotation concentrates have to be agglomerated before charging into the blast furnace.)

Sinter roasting is carried out in a Dwight-Lloyd sintering machine, as shown in Fig. 4.6. The fine concentrate is charged as a layer 15-50 cm thick on to an endlessly revolving belt of grates

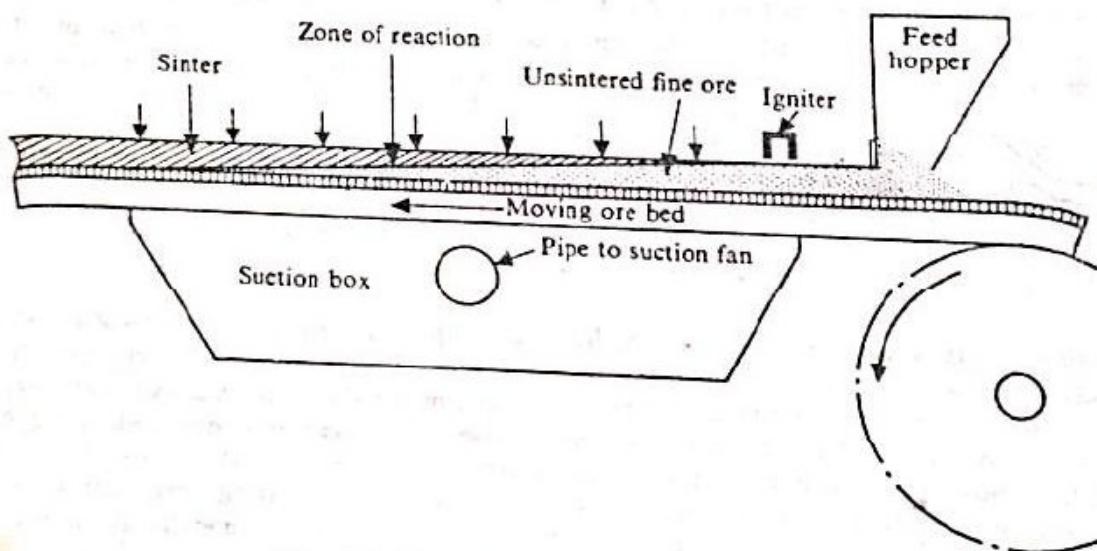


Fig. 4.6 Dwight-Lloyd Sintering Machine.

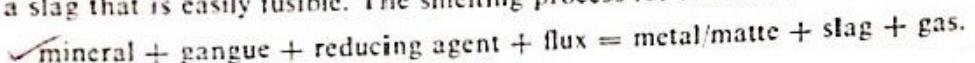
or pallets which moves over wind boxes at a regulated speed. A burner under the ignition hood is used to start the combustion of the bed surface. This combustion is then propagated through the mass of the charge by a current of air drawn through the charge into the wind box below which is connected a suction fan. Sufficiently high temperatures are developed in the material to cause partial or incipient fusion, which produces a porous cinder-like material called *sinter*. A certain amount of moisture is necessary to render the sinter porous. When the sinter reaches the end of the machine, it is discharged and cooled. The cooled sinter is sized to give a uniform product. The sinter roasting of a sulphide ore does not require the addition of any fuel to the charge because the sulphur in the charge itself acts as fuel. In the case of an oxide ore (e.g., iron ore), however, fuel has to be added.

Although a multiple hearth roaster is conventionally used in the case of zinc ores, sinter

roasting can also be used. However, in the case of copper ores, sinter roasting finds limited application because a reverberatory furnace can handle fine ores efficiently.

### 4.6 SMELTING

*Smelting* is a heating process for the production of a metal or matte. Generally, the process is one of reduction of the oxide of the metal with carbon/sulphur/sulphide in a suitable furnace (reverberatory furnace, blast furnace, or electric furnace). During smelting it should be remembered that since the gangue in the ore is generally less fusible than the metal, a flux must be added to form a slag that is easily fusible. The smelting process for metal extraction can be written as



Some of the general characteristics of a smelting operation are:

- (1) The materials to be smelted are usually charged in the solid state.
- (2) The products of the smelting furnace are in the liquid state; the solid material that escapes is the dust that is carried away by the furnace gases.
- (3) The heat required for smelting is usually supplied by external sources.

*Reduction smelting* is usually carried out in a blast furnace and *matte smelting* in either a reverberatory furnace or a flash smelter. Both reduction smelting and matte smelting can be carried out in an electric furnace. In reduction smelting, the ore is reduced by carbon, in the presence of a flux, to produce the molten metal and the slag. Sometimes, reduction is brought about by another metal whose oxides are much more stable than those of the metal being extracted. On the other hand, in *matte smelting*, a reducing agent is not used. The sulphide itself acts as a reducing agent. In this operation, metal is not produced; the products being molten matte and molten slag.

#### FLUXES

In smelting, a flux is used to lower both the liquidus temperature and the viscosity of the slag. A flux is classified according to the chemical type and chosen keeping in view criteria such as the chemical nature of the gangue and the properties desired in the slag such as density and viscosity. For a siliceous gangue, a basic oxide such as lime is commonly used as a flux and, for a basic gangue, an acidic oxide such as silica is used. When the flux has to act mainly as a 'cover', either potassium carbonate or sodium carbonate is used as a flux. Oxidizing fluxes such as  $\text{Na}_2\text{O}_2$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$ , and reducing fluxes, e.g.,  $\text{NaCN}$  are employed in the metallurgy of precious metals. A neutral flux ( $\text{CaF}_2$  or  $\text{Na}_2\text{SO}_4$ ) finds specialized application, for example, in fused electrolytic bath.

#### SLAGS

The two main functions of a slag are to collect the unreduced gangue minerals so as to form a separate layer in a metal extraction process and to provide a medium in which the impurities in a metal can collect during a refining process. (Often, the impurities get partitioned between the metal and the slag.) To effectively fulfil these functions, a slag must possess the following properties:

- (1) The difference between the specific gravities of the slag and the metal should be sufficiently high so that one can be easily separated from the other.
- (2) The slag must be fluid enough to permit its easy separation from the metal and also to

bring about a mass transfer faster (than when the slag is not fluid enough) of the reacting and product species. (If a slag is viscous, the loss of metal by entrapment in the slag is high.)

(3) The slag must have a chemical composition which ensures that the activities of the impurities and of the dissolved gangue minerals are low.

### REDUCTION SMELTING USING CARBON

Carbon occupies a unique position as a reducing agent mainly because it is easily available and, at the same time, it is inexpensive. It has already been shown in Chapter 2 that all metal oxides can, in theory, be reduced by carbon, provided the temperature is high enough.

The reduction of a metal oxide by carbon at high temperatures is often represented as



As represented by reactions (4.23) and (4.24), the reaction takes place between two solids, namely,  $MO$  and  $C$ . Since this reaction (which is a reduction) is controlled by solid-state diffusion across a small area of contact, it is likely to proceed at a slow rate. On the other hand, if the reduction takes place in more than one step, i.e., if there is an intermediate reaction between a gas and a solid, it is likely to proceed faster. The reduction can be represented more accurately than in reactions (4.23) and (4.24) as



Combining reactions (4.25) and (4.26), we get the overall reaction as



Thus, it would not be correct to state that reduction takes place according to reaction (4.23). This would probably be true in the reduction of the most stable oxides, where  $p_{CO}$ , in the resulting gas mixture would be extremely low. At a temperature lower than  $700^\circ C$ , the reduction can be represented by reaction (4.25).

The reduction of an oxide by carbon is best understood by referring to the Ellingham diagram (Fig. 2.1). Referring back to Fig. 2.1, we observe that the temperatures required for reduction by carbon in a number of cases are beyond practical limits. It is just possible to produce manganese or, at least an alloy of manganese (Fe-Mn), in a blast furnace. Metals lying above manganese in the emf series form oxides having higher negative free energies of formation and may be reduced by carbon but not in a blast furnace. For the reduction of these more stable oxides, an electric furnace is required because it can attain much higher temperatures.

During cooling (from the reacting temperature) a back reaction may occur, especially when the reduced metal is in the form of a vapour, as in the case of magnesium. Some metals, for example, zinc, can be condensed in the presence of  $CO$ , where the back reaction is limited to a great extent. However, the more reactive metals react with the  $CO$  itself when the gas mixture is cooled. For example, the back reaction in the case of magnesium has to be restrained by shock

cooling. The resulting powder, however, is pyrophoric, i.e., it ignites on contact with air. Some alkaline earth metals form carbides, for example,  $\text{CaC}_2$ .

At high temperatures, fresh problems may arise. For instance, a new stable phase, namely, the metallic carbide, may appear. This is sometimes formed when the metal reacts with the carbon itself. The formation of carbide can be suppressed if the metal were produced in the presence of another solvent metal. To illustrate: the solvent metal, in which a metal M is dissolved, reduces the chemical potential of M and pushes the reduction reaction (4.23) to the right, making reduction possible at a lower temperature. The greater the dilution, the lower is the temperature required for reduction. For the same reason, carbide formation would be discouraged if M were in the form of an alloy, for example, the production of a Be-Cu alloy (with about 4 per cent copper) by carbon reduction of  $\text{BeO}$ . The production of ferroalloys also makes use of the advantage gained by alloying. Ferrovanadium, ferrotitanium, ferrosilicon, ferroniobium, and other ferroalloys are produced by the reduction of the corresponding oxide by carbon in the presence of iron. Even alloying does not always ensure a carbide-free product. For example, ferrochromium normally contains a high proportion of carbon, the composition approaching  $\text{Cr}_4\text{C}(\text{Fe})$ . Special techniques are, therefore, necessary to produce low-carbon alloys.

#### 4.7 METALLOOTHERMIC REDUCTION OF OXIDES

An oxide is reduced by a metal that forms stabler oxides. Such a metallothermic reaction, carried out in an open container or a closed container (bomb), completely avoids carbon contamination. Although the principle is similar to that of carbon reduction, metallothermic reduction is usually carried out on a small scale and is rarely referred to as smelting.

The principle of metallothermic reduction can be understood by referring again to the free energy diagram for oxides (Fig. 2.1). In theory, a metal that forms a stabler oxide (a lower line in Fig. 2.1) would replace metals from less stable oxides (an upper line in Fig. 2.1). In practice, however, the reduction would depend on factors such as the reaction rate and the physical properties of the reactants and products. For example, in the thermit reduction



the products are in a liquid state at the reaction temperature and all the constituents are relatively nonvolatile.  $\text{Al}_2\text{O}_3$  can be slagged more easily by using another oxide as a flux. A wide difference between the densities of the slag and the metal allows a clean separation. However, such a clean separation becomes difficult in the case of some other reductions, for instance, the reduction of  $\text{TiO}_2$  by calcium. The reaction is



It should be noted that titanium melts at  $1670^\circ\text{C}$ , calcium boils at  $1492^\circ\text{C}$ , and  $\text{CaO}$  melts only at  $2600^\circ\text{C}$ . A liquid product can be obtained only if these high temperatures can be attained, i.e., the application of a very high pressure becomes necessary. The final product is normally a mixture of solid titanium and  $\text{CaO}$ ; the latter can be leached out and the metal obtained in a powder form. This powder can subsequently be melted and thus consolidated. However, during remelting, sufficient precaution must be taken to avoid oxygen contamination because any residual  $\text{CaO}$  can easily oxidize the titanium metal, rendering it brittle.

It should be remembered that the free energy diagram (Fig. 2.1) is plotted for 1 atm

of oxygen. The order of reactivity of oxides can be changed by applying a vacuum. Thus, under vacuum, silicon can reduce  $MgO$  and aluminium  $CaO$ , although the reverse is expected under standard conditions. The chemical potential of magnesium is reduced by 17.5 kcal per mole at  $1000^{\circ}C$  by operating at about 0.001 atm, and, at the same temperature and under the same pressure the free energy change for the reduction of  $MgO$  by Si is rendered negative (see Chapter 6).

### FORMATION OF SLAG

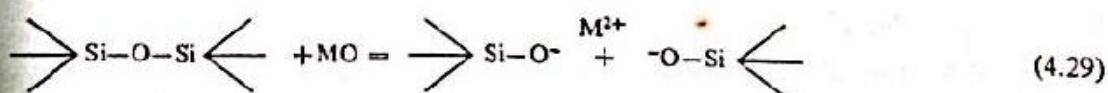
The reduction of a metal oxide by a metal necessarily results in a more stable, often highly refractory, oxide. Although carbon reduction does not produce a condensed oxide phase, it releases siliceous material or other gangue materials from the ore to form a refractory oxide phase. It is desirable to have a liquid slag so that the metal can be easily separated from the gangue. The formation of a liquid slag is facilitated by adding, to the ore, fluxing agents such as quartz and lime, which together with the gangue (the product oxide for metallocermic reduction), form a multicomponent silicate slag with a relatively low melting point.

All silicate melts are viscous. To facilitate their removal, their viscosity should be decreased either by adding a suitable basic oxide or by raising the temperature. The effect of adding a basic oxide and of raising the temperature can be understood from the structure of molten silicates. Due to the industrial importance of metallurgical slags (most of which are multicomponent silicate solutions), the structure and constitution of molten silicates have been investigated. Consequently, several theories on silicate structure have been proposed. It is now accepted that silicate melts are ionic in nature. In a silicate solution, there could be metallic ions, free oxygen ions, and complex silicate ions of varying sizes. However, there cannot be a silicon ion. A high degree of stability of the  $Si-O$  bond requires that every silicon atom always be tetrahedrally coordinated with four oxygen atoms. The viscosity of a slag essentially depends on the bulky, less mobile silicate ions, which decrease the overall fluidity.

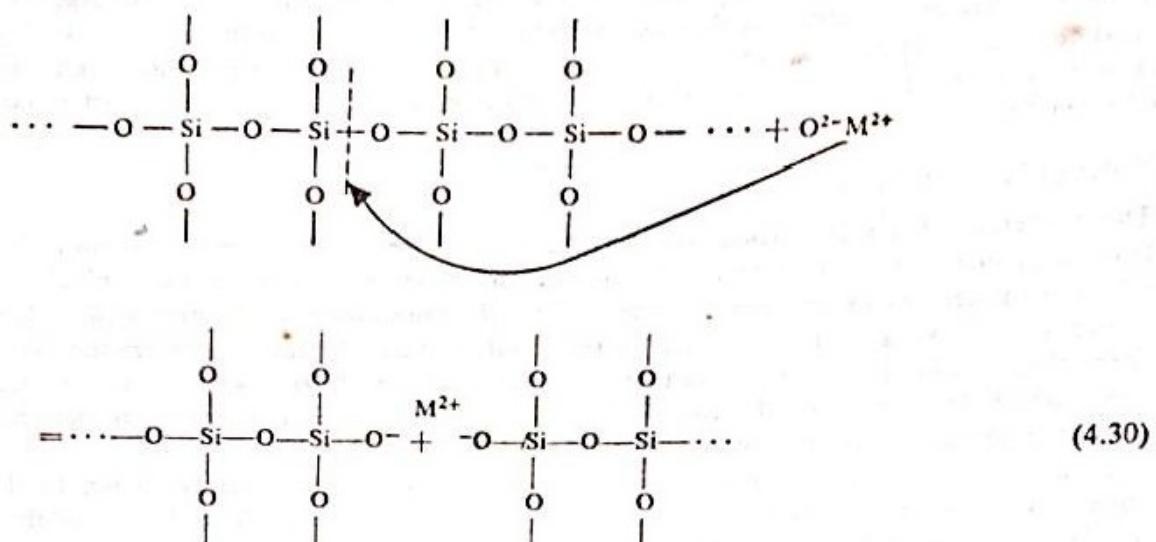
### STRUCTURE OF SILICATE SLAGS

Consider now the variation in the silicate solution structure over a range of silicate compositions. For simplicity, consider a binary silicate system  $MO-SiO_2$ . The structure of pure crystalline silica is a three-dimensional network consisting of silicon and oxygen atoms (where each silicon atom is tetrahedrally attached to four oxygen atoms) possessing both long-range order and short-range order. Therefore, the entire bulk of the material could, in effect, be a huge molecule, i.e., a single unit. In molten silica, however, some  $Si-O-Si$  bonds rupture due to the effect of thermal energy and some depolymerization takes place. The short-range order persists, even though the long-range order is lost. In such a situation, the viscosity is very high.

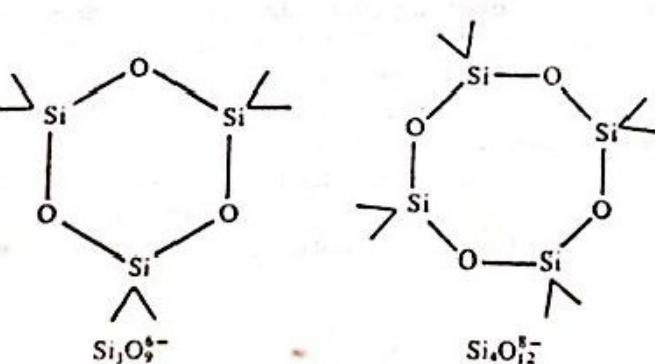
When a basic metal oxide  $MO$  (e.g.,  $CaO$ ,  $MgO$ ) is added to molten silica, the three-dimensional network starts breaking. This is attributed to the reaction of the oxygen ions provided by the metal oxide with the  $Si-O$  bond in the network as shown in reactions (4.29) and (4.30):



05



Here, silica (acidic oxide) accepts an oxygen ion and MO (basic oxide) donates an oxygen ion. The depolymerization reaction (4.29) essentially shows that as the quantity of the metal oxide added (i.e., the quantity of oxygen ions) increases, the silicate network is broken down into smaller and smaller units. The basic reaction is one that involves doubly bonded oxygen atoms in the network ( $O^0$ ), the free oxygen ion donated by MO ( $O^{2-}$ ), and the single bonded or terminal oxygen atoms ( $O^-$ ) in the smaller units produced. The reaction is



When even more metal oxide is added, more oxygen bridges break. Finally, at the composition  $\text{MO : SiO}_2 = 2 : 1$  (as in the orthosilicate  $2\text{MO} \cdot \text{SiO}_2$ ), the smallest unit  $\text{SiO}_4^{4-}$  is obtained. When

further metal oxide is added, free oxygen ions ( $O^{2-}$ ) become available in the melt.

From the foregoing discussion, it is obvious that the addition of a basic oxide lowers the viscosity of a slag because it leads to depolymerization and creates smaller flow units, which are more mobile. It should be noted that depolymerization can be brought about by raising the temperature. Thermal bond breaking is greater at higher temperatures.

### METAL LOSSES IN SLAGS

A serious complication could arise during smelting if the reactant and product oxides themselves form compounds. This possibility exists for an oxide ore that can form a stable silicate itself. Although this situation could sometimes be advantageous in producing slags with a low melting point, it indicates that a part of the reactant raw material would be lost due to dissolution in the slag along with the gangue and fluxes. Metal recovery, consequently, would be low. For example, during the blast furnace smelting of a lead ore, a significant quantity of  $PbO$  may combine with silica to enter the slag as a silicate. This  $PbO$  loss can be minimized by adding scrap iron to the charge. Scrap iron not only reduces some of the  $PbO$  itself but also helps recover lead from the silicate slag. The reactions can be written as



The reduction of  $SnO_2$  also creates a problem similar to that of  $PbO$  because the oxide itself can form a stable silicate. Consequently, tin cannot be easily recovered, and special multistage smelting techniques must be adopted in which the tin-rich slag itself is smelted in various stages. The reduction temperature for a tin-bearing slag is around  $1250^\circ C$  as against a much lower temperature for  $SnO_2$  ( $500^\circ C$ ). Consequently, smelting operations have to be carried out at around  $1250^\circ C$ . The metal is also lost as a result of mechanical entrapment in slags.

### CLASSIFICATION OF SLAGS

Slags used in smelting are sometimes classified according to the silicate degree defined as

$$\text{silicate degree} = \frac{\text{moles of acidic oxygen from } SiO_2}{\text{moles of basic oxygen from } CaO, MgO, FeO, \dots}.$$

#### Basic Slags

According to the foregoing definition of the silicate degree, a basic slag has a silicate degree  $< 1$  and corresponds to the composition  $MO/SiO_2 > 2$ . The principal anions in a molten basic slag are  $O^{2-}$  and  $SiO_4^{4-}$ .

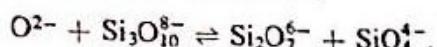
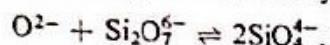
#### Neutral Slags

A neutral slag has a silicate degree = 1 and corresponds to the composition  $MO/SiO_2 = 2$ . The principal anion in a molten neutral slag is  $SiO_4^{4-}$ .

#### Acid Slags

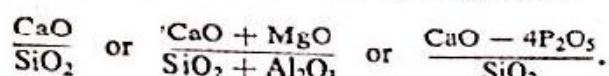
An acid slag has a silicate degree  $> 1$  and corresponds to the composition  $MO/SiO_2 < 2$ . The principal anions in an acid slag are the chain silicate anions  $Si_2O_7^{6-}$ ,  $Si_3O_{10}^{8-}$ , the ring silicate anions  $Si_4O_{12}^{8-}$ , and the other globular anions.

It should be pointed out that in a melt, irrespective of the composition, there exists an equilibrium among the various types of anions. For example, some equilibria that can exist are



Consequently, some free oxygen ions—although in very small quantities—can be present in a neutral slag and even in an acid slag.

In industrial practice, the basicity of a slag is sometimes expressed in terms of a basicity number called 'V ratio' and defined by the % ratios



A basic slag contains a high proportion of lime and an acid slag a high proportion of silica. The relative basicity of a slag can be expressed in terms of these ratios.

#### 4.8 SMELTING FURNACES

The blast furnace has traditionally been the most popular furnace for reduction smelting. Smelting of iron ores is the best known example of blast furnace operation. Lead is also almost exclusively produced in the blast furnace. In this case, however, the furnace is much smaller. The imperial smelting process has been developed in England for the simultaneous production of lead and zinc in the blast furnace. While lead is tapped, as is normally done, zinc is recovered by dissolving the outgoing zinc vapours in a running stream of hot molten lead. Zinc separates from lead on cooling. The blast furnace in this case must have special arrangements at the top for the collection and dissolution of the zinc vapours. There should also be a provision for the flow of a stream of molten lead which is continuously recirculated after zinc recovery.

In blast furnace smelting, strongly reducing conditions can be created, but where reducing conditions are unnecessary or undesirable, a simpler furnace such as a reverberatory furnace should be used. For example, in tin smelting, tin oxide should be smelted in a reverberatory furnace so as to minimize the reduction of the more stable oxide impurities such as iron oxides.

When very high temperatures are required for reduction and fusion, electric arc smelting is employed. A temperature around  $2000^{\circ}\text{C}$  can be easily attained in an electric furnace whereas carbonaceous fuels (used in the blast furnace) usually cannot provide temperatures higher than  $1600^{\circ}\text{C}$ . Therefore, ferroalloys that require very high temperatures for reduction are smelted in the electric furnace. Figure 4.7a depicts an iron blast furnace, Fig. 4.7b a reverberatory furnace, and Fig. 4.7c a direct arc electric furnace.

No special furnace is required for the metallothermic reduction of an oxide. The need for an external heat source is limited because, in the reduction of an oxide, the reactions are highly exothermic. Their exothermicity can be enhanced by incorporating booster reactions. A simple unit for metallothermic reduction is shown in Fig. 4.8.

#### FLASH SMELTING

In recent years, one of the most interesting developments in smelting has been the *flash smelting* of the concentrates of nickel sulphide and copper sulphide. Flash smelting is a process that combines the operations of flash roasting and smelting. The object is to burn the concentrate

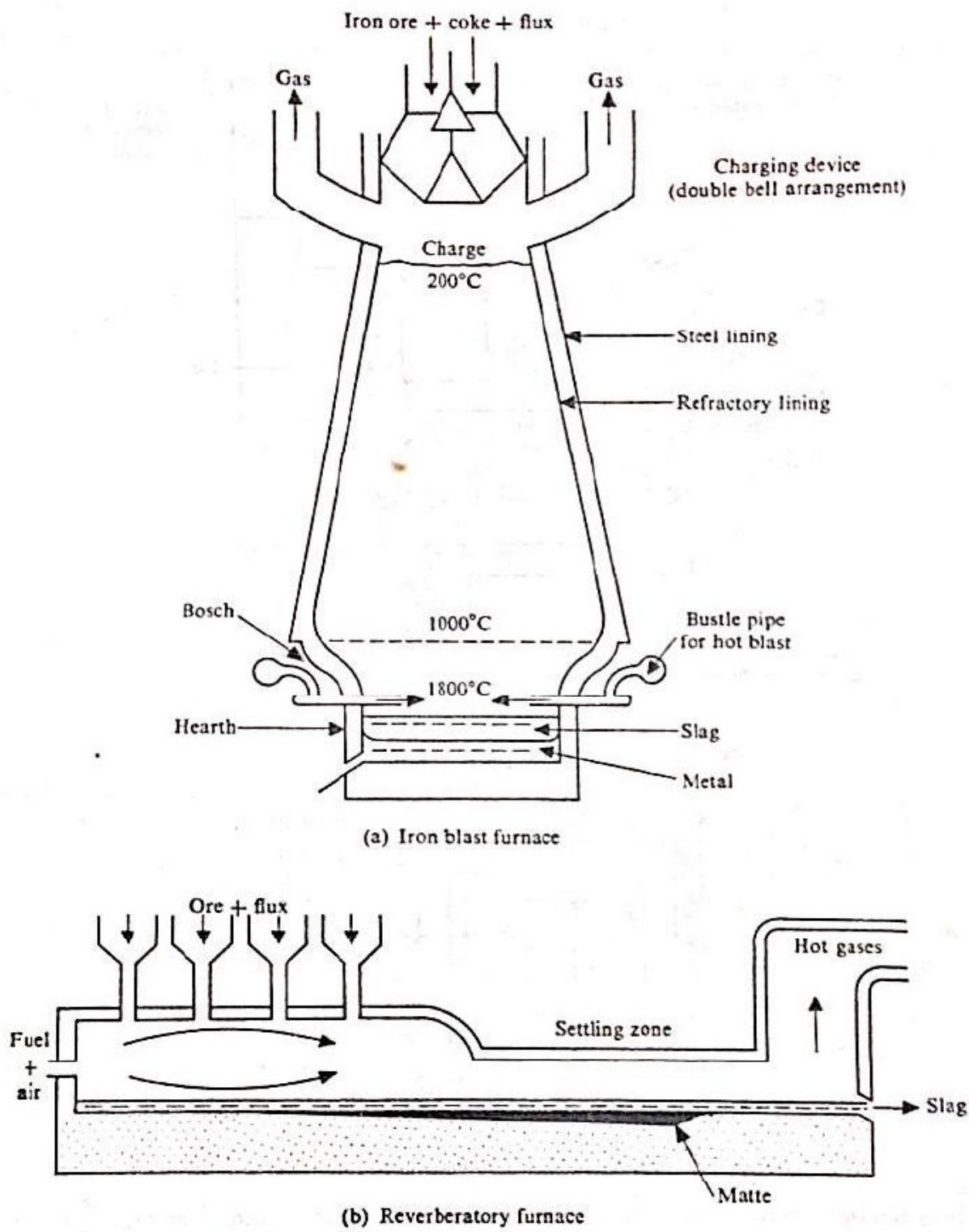
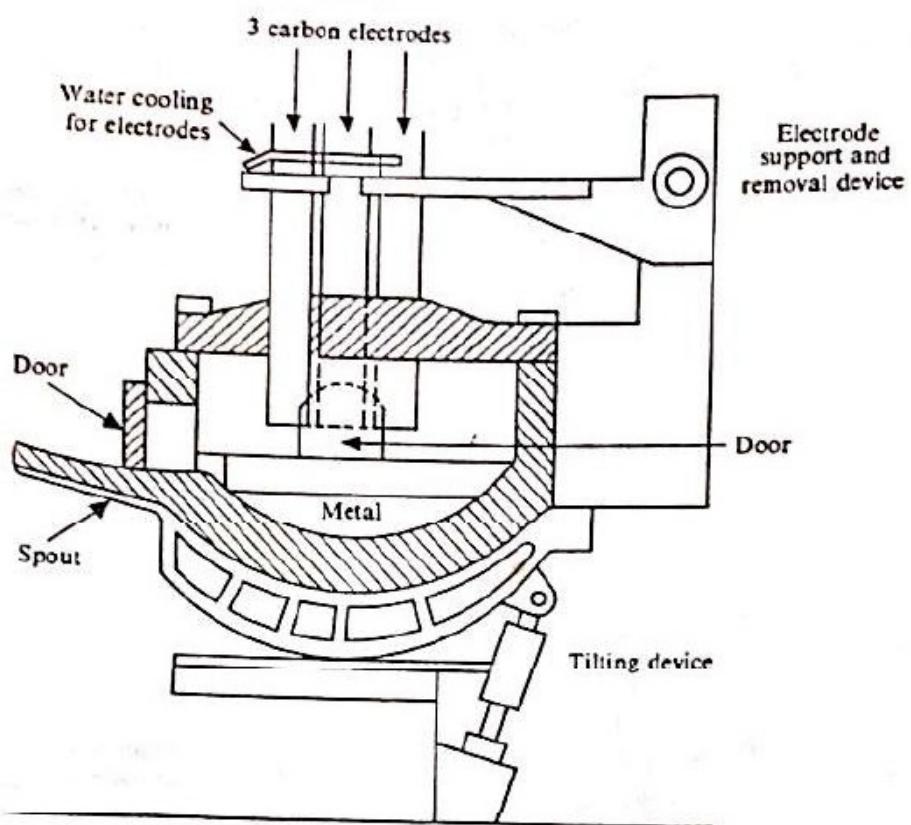


Fig. 4.7 Types of Smelting Furnaces (cont.).



(c) Direct arc electric furnace

Fig. 4.7 Types of Smelting Furnaces.

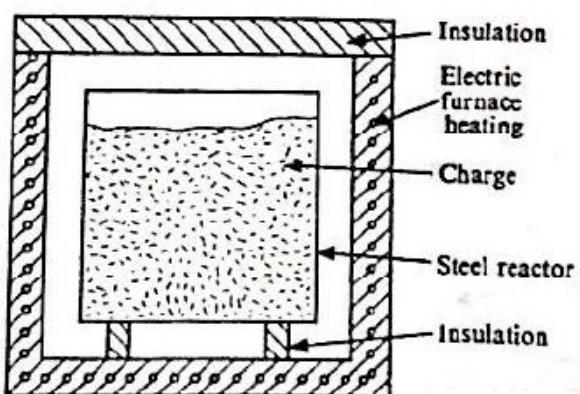


Fig. 4.8 Unit for Metallothermic Reduction.

(falling through the combustion chamber of a flash smelter) with oxygen or preheated air blown in with the concentrate. Sufficient heat is generated to form a matte and a slag which settle into the hearth.

In flash smelting, enriched preheated air or pure oxygen is usually used instead of air to increase the combustion rate and to maintain autogenous smelting. The gases coming out of the furnace are very rich in  $\text{SO}_2$  (due to the high combustion rate) and can be profitably used for sulphuric acid manufacture. A flash smelter is illustrated in Fig. 4.9.

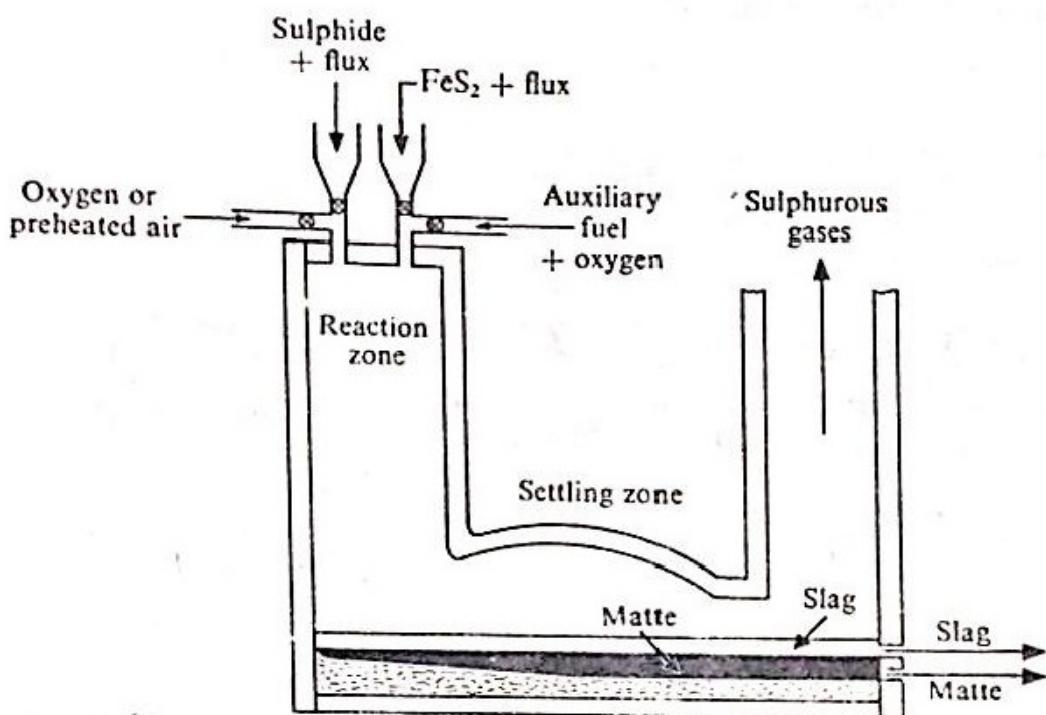


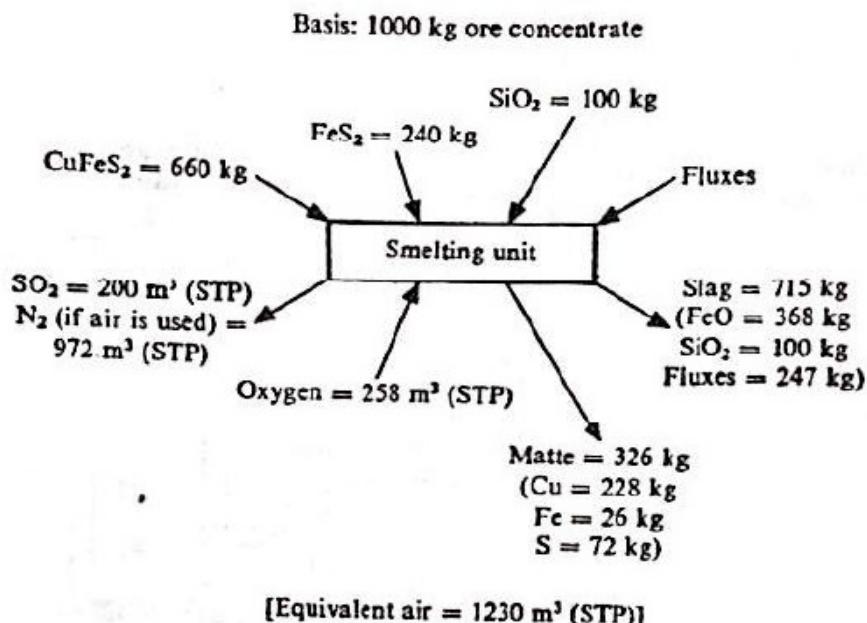
Fig. 4.9 Flash Smelter (after Gilchrist, 1967).

Flash smelting, like flash roasting, can be made autogenous, provided the exothermic heat and the sensible heat of the incoming feed materials combine to exceed the heat losses. Generally, when air is used as an oxidant, it has to be preheated. For oxygen-enriched air, the required preheating would obviously be lesser. For flash smelting with air, the extent of preheating required can be easily calculated by performing a mass and energy balance. We now give a simple example.

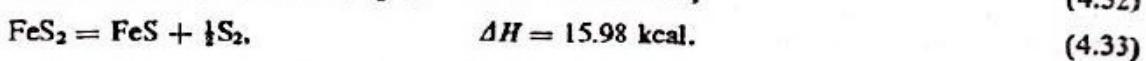
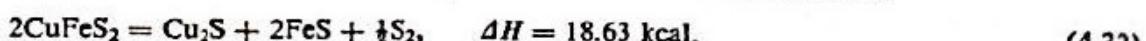
Let us assume that the concentrate used for flash smelting has the composition: chalcopyrite ( $\text{CuFeS}_2$ ) 66 per cent; pyrite ( $\text{FeS}_2$ ) 24 per cent; and gangue ( $\text{SiO}_2$ ) 10 per cent. Let us also assume that flash smelting produces a copper matte containing 70 per cent Cu, 8 per cent Fe, and 22 per cent S and a slag containing 40 per cent Fe. The matte, slag, and gases leave the furnace at, say, 1300°C.

To begin with, we must know the compositions of all the phases involved in the smelting operation. Their compositions can be easily obtained from mass balance calculations. To calculate the amount of oxygen required, we should know both the quantity of sulphur oxidized to  $\text{SO}_2$  which does not enter the matte phase and the quantity of oxidized Fe which enters the slag phase as  $\text{FeO}$ . Calculations are based on the smelting of 1000 kg of ore concentrate and it is assumed that the relevant reactions are given by (4.32)–(4.34) as described for the heat balance calculations. From reactions (4.32)–(4.34), we see that 57.4 kg of oxygen are required to oxidize

the free sulphur from 660 kg of  $\text{CuFeS}_2$  and 64 kg of oxygen are required to oxidize the free sulphur from 240 kg of  $\text{FeS}_2$ . We also note that 492 kg of  $\text{FeS}$  are formed of which 41 kg go into the matte. For oxidizing the remaining 451 kg of  $\text{FeS}$ , according to the reaction represented by (4.35), 246 kg of oxygen are required. Therefore, the total oxygen requirement is 367.4 kg or 258  $\text{m}^3$  (STP). The results of the mass balance are diagrammatically shown now:



We next proceed to make an inventory of the heat input and output on the basis of thermochemical data available from standard sources. To calculate the heat balance, we assume that  $\text{CuFeS}_2$  and  $\text{FeS}_2$  first dissociate to give  $\text{FeS}$  and  $\text{S}_2(\text{g})$ , which subsequently burn with the oxygen supplied to produce oxides of iron and sulphur. The dissociation reactions are



The free sulphur vapour, on oxidation to  $\text{SO}_2$ , generates heat according to the reaction



The total heat absorbed by  $\text{CuFeS}_2$  and  $\text{FeS}_2$  for decomposition is

$$\left(\frac{660,000}{2 \times 184}\right)18.63 + \left(\frac{240,000}{120}\right)15.98 = 65,500 \text{ kcal}.$$

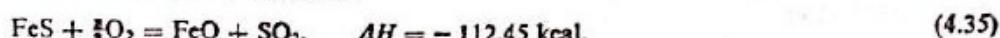
The total heat evolved due to the oxidation of sulphur is

$$\frac{1000}{32} \left[ \left(\frac{32}{2 \times 184}\right)660 + \left(\frac{32}{120}\right)(240) \right] (70.9) = 270,000 \text{ kcal}.$$

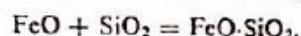
Hence, the net heat produced during sulphur oxidation is

$$(270,000 - 65,500) \text{ kcal} = 204,500 \text{ kcal}.$$

The oxidation of  $\text{FeS}$  can be written as



Matte contains 26 kg of Fe or 41 kg of  $\text{FeS}$  and the remainder is oxidized to  $\text{FeO}$ . By mass balance, the total weight of  $\text{FeS}$  is 451 kg (Fe = 286 kg) and the heat evolved on the oxidation of  $\text{FeS}$  is  $(451,000/88) 112.45 = 577,000$  kcal. The  $\text{FeO}$  formed in reaction (4.35) reacts with  $\text{SiO}_2$  to form a slag  $\text{FeO} \cdot \text{SiO}_2$  according to the reaction



Suppose this reaction liberates 100 kcal of heat per kg of iron, then, the heat liberated due to slag formation is 28,600 kcal. Thus, the total heat liberated is  $(204,500 + 577,000 + 28,600 =) 810,100$  kcal.

It is assumed that all reactions occur at  $25^\circ\text{C}$  and the products of the reaction are heated to the final temperature by the heat generated by the reactions.

To estimate heat losses, we assume that the matte, slag, and gases, among them, carry away the entire heat generated in the furnace at  $1300^\circ\text{C}$ . In practice, the heat from the furnace that escapes into the atmosphere also must be taken into account. We now give some estimates of heat losses (based on the values available in the literature):

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} \text{ (matte)} = 222 \text{ kcal/kg.}$$

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} \text{ (slag)} = 340 \text{ kcal/kg.}$$

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} \text{ (SO}_2\text{)} = 714 \text{ kcal/m}^3,$$

$$H_{1300^\circ\text{C}} - H_{25^\circ\text{C}} \text{ (N}_2\text{)} = 445 \text{ kcal/m}^3.$$

Thus,

$$\text{heat lost through matte} = 222 \times 326 = 72,300 \text{ kcal,}$$

$$\text{heat lost through slag} = 340 \times 715 = 243,100 \text{ kcal,}$$

$$\text{heat lost through SO}_2 = 200 \times 714 = 142,800 \text{ kcal,}$$

$$\text{heat lost through N}_2 = 972 \times 445 = 432,500 \text{ kcal.}$$

Assume that heat loss through radiation and convection is 100,000 kcal. Therefore, the total heat loss is 990,700 kcal.

The heat balance is shown as:

	Heat input (kcal)	Heat output (kcal)	
Oxidation of sulphur	204,500	Lost through matte	72,300
Oxidation of $\text{FeS}$	577,000	Lost through slag	243,100
Formation of slag	28,600	Lost through $\text{SO}_2$	142,800
		Lost through $\text{N}_2$	432,500
		Lost due to radiation and convection	100,000
Total	810,100	Total	990,700

Therefore, the heat deficit is  $(990,700 - 810,100 =) 180,600$  kcal.

This deficit can be made up by preheating the air used for combustion. The heat deficit per  $m^3$  of air =  $180,600/1230 = 146$  kcal. Thus, every  $m^3$  of air input must be supplied with 146 kcal of heat prior to reaction. If air is preheated to  $458^\circ\text{C}$ , this enthalpy is made up and the total heat input is 990,700 kcal. It should be noted that the heat carried away by gases is  $(575,300/990,700)100$ , i.e., 58 per cent of the total heat input. The gases that come out of the furnace, therefore, have sufficient heat to preheat the incoming air. This heat should be utilized by employing a suitable heat recovery unit. We may thus conclude that theoretically there is no difficulty in carrying out autogenous smelting. Starting with a rich copper concentrate, we should obtain a relatively rich matte. The grade of the matte can also be controlled by regulating the amount of air or oxygen, whichever is being injected.

#### 4.9 MATTE SMELTING

In the extraction of a metal from a sulphide ore, an important method used involves the production of a liquid matte from the ore and its subsequent conversion to the metal. In matte smelting, the sulphide ore is fused with a flux to produce a molten mixture of sulphides known as a *matte*. The gangue materials pass off into the slag, which is immiscible with the matte, i.e., it forms a separate layer. Some sulphur is lost in the furnace gases as  $\text{SO}_2$  or  $\text{SO}_3$ . In this sense, for a sulphide ore, matte smelting is a thermal concentrating process.

A matte is a metallic sulphide solution that contains minor amounts of oxygen and, sometimes, some metal too. A matte exhibits a high electrical conductivity comparable with that of a metal and has a density in between the density of the metal and that of the slag. Mattes, in general, are insoluble in the metal and slag phases. Thus, in some processes three distinct layers, namely, slag, matte, and metal are produced. A matte is an excellent solvent for some impurity metals, especially for valuable traces of precious metals.

Matte smelting, which is usually carried out in a reverberatory furnace, follows a roasting operation. Roasting first reduces the sulphide content of an ore in such a manner that subsequent smelting with a suitable flux produces a matte of the required grade. It should be noted that roasting brings about only the partial oxidation mainly of  $\text{FeS}$  and  $\text{FeS}_2$  to  $\text{FeO}$ , which would pass off into the slag phase.

Matte smelting is adopted in the extraction of copper, nickel, and, sometimes, antimony. The common ores of these metals contain sulphide minerals including  $\text{FeS}$ . During roasting, prior to matte smelting, the sulphides of iron are oxidized more easily than those of copper and nickel. The oxidation of, say,  $\text{Cu}_2\text{S}$  or  $\text{Ni}_3\text{S}_2$  can be avoided by controlling the oxidation of the ore so as to produce only  $\text{FeO}$  and not  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . This is necessary because the higher oxides of iron do not pass off into the slag easily and are thus difficult to remove. Copper is subsequently recovered from the matte by a process known as 'converting' in which air is blown through a side-blown converter. Initially, the residual  $\text{FeS}$  is oxidized and slagged out. Subsequently, the sulphides of copper are converted to metallic copper. For a nickel matte the procedure is somewhat more complicated. (Matte smelting of copper and nickel is discussed in detail in Chapter 7.)

#### 4.10 REDUCTION OF HALIDE BY ANOTHER ELEMENT

A number of rare and reactive metals are produced by the reduction of a halide by another metal. The basic reaction is



where  $M$  and  $M'$  are two different metals,  $X$  is a halogen (usually fluorine or chlorine), and  $n$  the number of atoms of  $X$ . Earlier, reaction (4.36) had been the basis for the extraction of reactive metals. Presently, however, this method is almost exclusively employed only for a few metals, for example, titanium and zirconium. Kroll's process employed for the reduction of a halide using magnesium is an example of this method. The reaction is



In reaction (4.37), sodium may be used instead of magnesium.

The principle of halide reduction can be understood from a chloride free energy diagram (Fig. 4.10), which is similar to that relating to oxides (Fig. 2.1). Figure 4.10 is drawn for the formation of chlorides from 1 gm mole of chlorine for each of the reactions represented. In this figure, elements such as Na, K, Li, Ca, and Mg appear at the bottom because their halides are very stable. These metals are, therefore, excellent reducing agents.

The melting, boiling, and sublimation points of the chloride are designated as  $M$ ,  $B$ , and  $S$ , respectively, and those of the metals as  $M'$ ,  $B'$ , and  $S'$ , respectively. The reversible decomposition voltage  $E$ , given by  $\Delta G^\circ = -ZFE$ , is indicated on the left-hand side of the figure. The position of the line for  $\text{CCl}_4$  clearly shows that carbon is not a suitable reducing agent for chlorides.

The lines for most chlorides have an upward slope, whereas the  $\text{HCl}$  line has a slight downward slope. This shows that hydrogen becomes a slightly better reducing agent at higher temperatures. Hydrogen can reduce all metallic chlorides whose lines lie above the  $\text{HCl}$  line, provided all the substances involved are in their standard states. Those metals whose chloride lines lie below the  $\text{HCl}$  line, when made to react with  $\text{HCl}$  gas, are converted to chlorides under standard conditions.

Halides usually have relatively low melting and boiling points which account for the interest of metallurgists in halide systems. If the metal produced at the reduction temperature is itself in a liquid state, then a clean liquid-liquid separation of the metal and slag is easily obtained, for example,



However, the melting points of reactive metals are generally high and these metals may be obtained in the form of a solid entrapped in a mass of slag. The situation is sometimes improved by incorporating booster reactions during bomb reduction so as to provide sufficient exothermic heat to melt the whole charge and thereby obtain a clean separation.

#### 4.11 HALIDE METALLURGY AND HALOGENATION

Halogens, particularly chlorine, are beginning to play an increasingly important role in extraction processes. Since halides are seldom found as natural ore deposits on land, they are produced from naturally occurring minerals by halogenation. The most commonly used halides are chlorides and fluorides. A chloride is preferred to a fluoride because it is less corrosive and is normally easier to handle. On the other hand, many chlorides are hygroscopic whereas fluorides are not; therefore, in some processes, for example, fused salt electrolysis, fluorides are preferred to chlorides.

Halogenation, particularly chlorination is carried out to achieve one or more of the objectives now listed:

- (1) 'Opening up' of relatively complex minerals and the recovery of the metallic values.
- (2) Beneficiation of low-grade ores to yield the metal halide, either in the vapour state or in

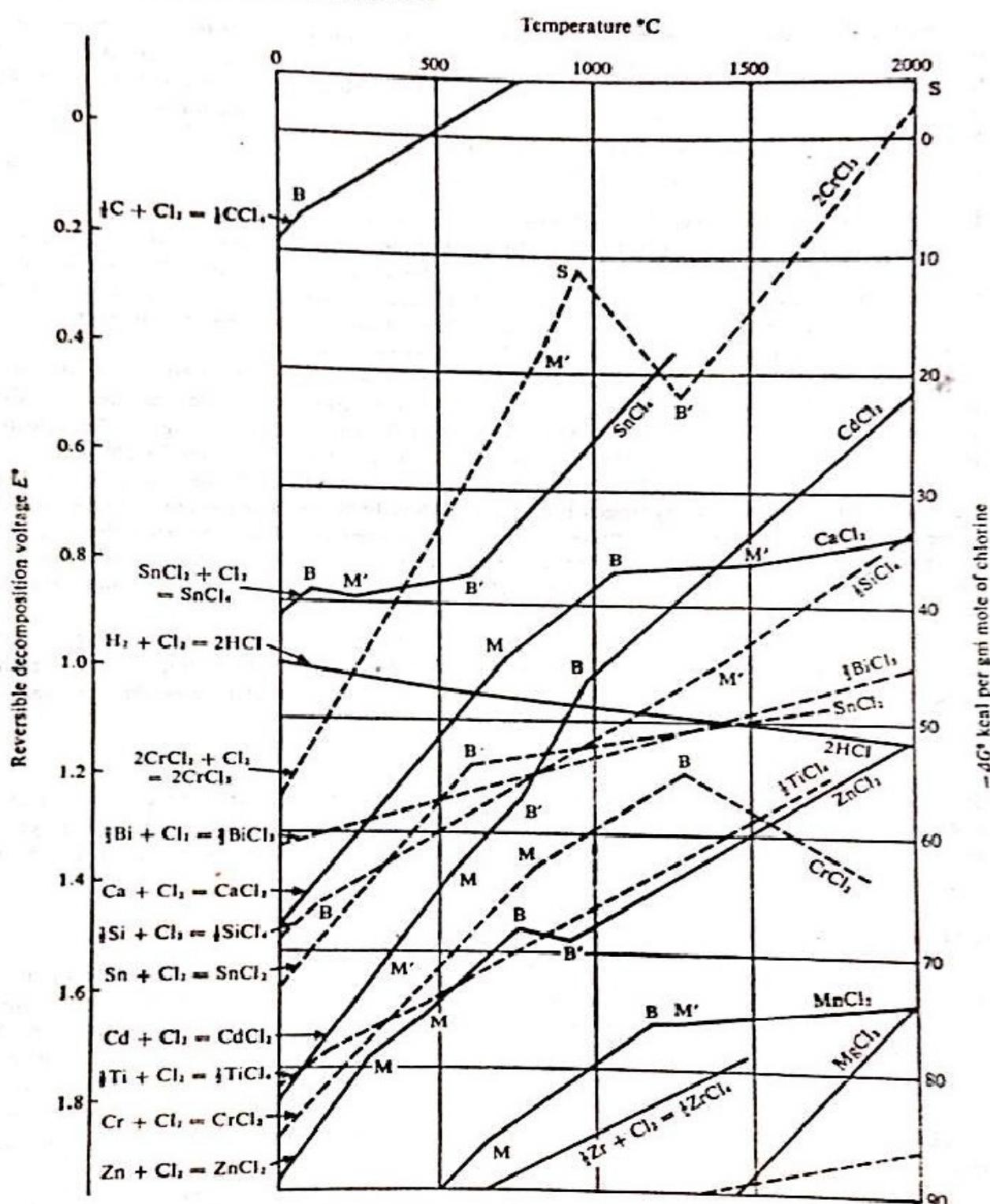


Fig. 4.10 Free Energy of Formation of Chlorides (after Kellogg, 1950) (cont.).

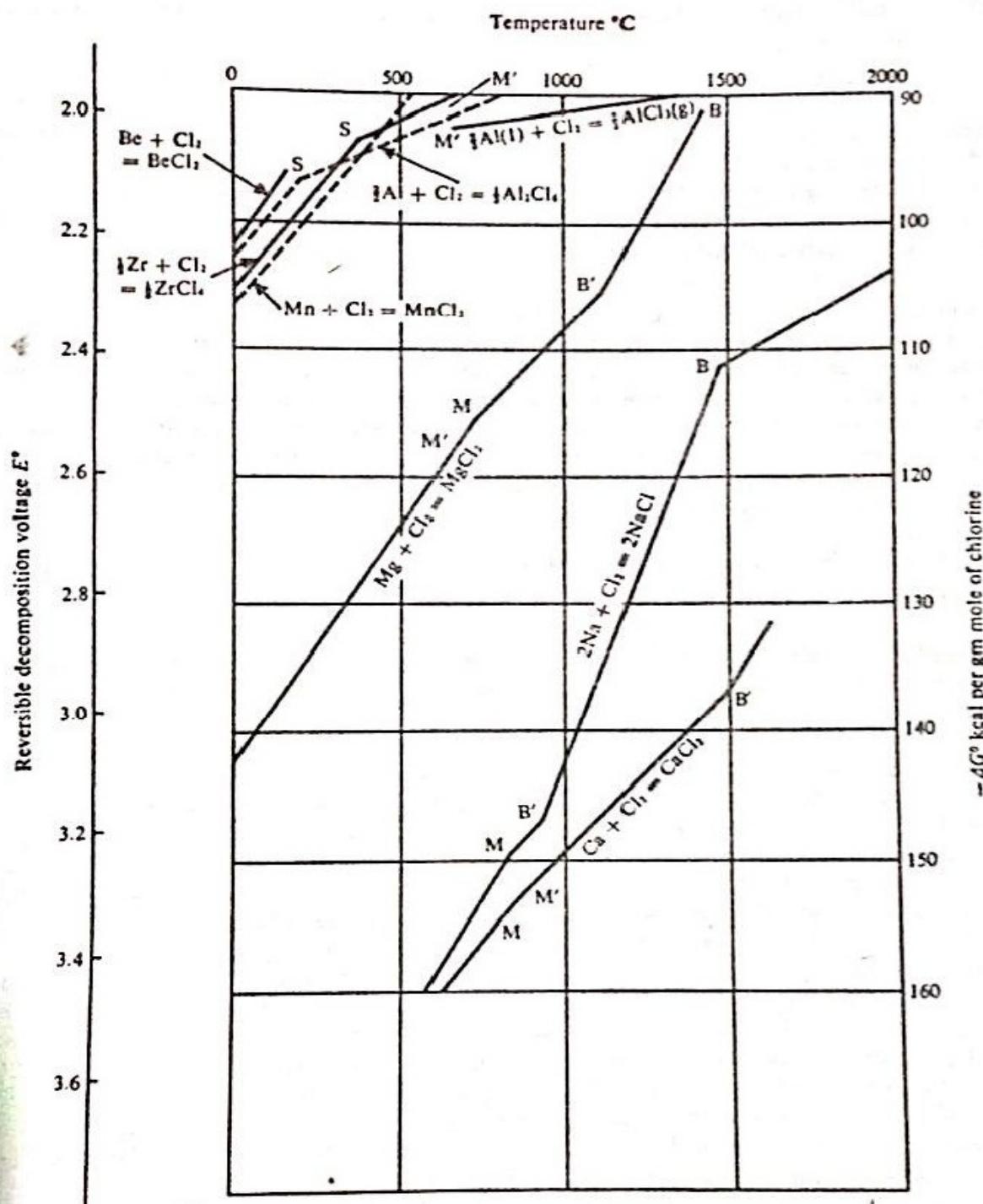


Fig. 4.10 Free Energy of Formation of Chlorides (after Kellogg, 1950).

the condensed state. A chloride can be effectively separated from the gangue materials and processed for the production of the metal. Many metallurgical wastes can also be chlorinated for subsequent metal recovery.

(3) Production of pure halides of reactive metals from which oxygen-free metal can be obtained. Reactive metals such as U, Th, Ti, Be, and Zr, if produced from oxides, may contain appreciable quantities of oxygen which is detrimental to their properties. The problem is largely solved by employing a halide route for extraction. (A metal can be produced from a halide by various processes, for example, the metallothermic reduction of a chloride, fused salt electrolysis, and the vapour transport process. These processes are discussed in detail in chapters dealing with the extraction of individual metals.)

(4) Refining of crude metals.

Examples of the uses of halogenation in refining reactions are discussed later in this chapter.

We now consider the foregoing objectives in a little more detail, with particular reference to chlorination. Chlorination processes can be conveniently categorized into three types, namely, chloridizing roasting, chloridizing volatilization, and chlorination in fused salts.

In chloridizing roasting, the ore is roasted with common salt and the solid chloride is recovered by leaching. This method is ideal for a sulphide ore where the roasting reaction is autogenous. For an oxide ore, the roasting reaction is facilitated by the addition of elemental sulphur. The reactions may be written as



Reaction (4.39) can also represent the chlorination of a carbonate that decomposes on heating. Sulphates and silicates may decompose sodium chloride by the direct interchange of the elements and radicals without the addition of sulphur.

In chloridizing volatilization, chlorination is carried out at temperatures relatively higher than in chloridizing roasting, and the chloride is recovered by volatilization. The elimination of the reaction products is particularly easy in the case of highly volatile chlorides such as those of Zr, Ti, and Be. Special problems may be encountered if a metal has a variable valency. For example, chlorination of chromium ores tends to produce both  $\text{CrCl}_2$  and  $\text{CrCl}_3$ . The boiling point of  $\text{CrCl}_2$  ( $1302^\circ\text{C}$ ) is higher than that of  $\text{CrCl}_3$  ( $943^\circ\text{C}$ ), and the former may plug up the chlorinator, if chlorination is not carried out at a sufficiently high temperature. The problem is solved by using a slight excess of chlorine at  $1000^\circ\text{C}$  so that only  $\text{CrCl}_3$  is produced.

Many chlorides are susceptible to oxidation by air or oxygen, especially at elevated temperatures. The susceptibility to oxidation of some chlorides at red heat has been investigated by several workers. The chlorides may be arranged in an increasing order of susceptibility as follows:  $\text{AgCl}$ ,  $\text{HgCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{LiCl}$ ,  $\text{MnCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CrCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{AlCl}_3$ , and  $\text{SiCl}_4$ . Many of these chlorides are also strongly hygroscopic and readily react with the moisture in air. During chloridizing volatilization, oxidizing conditions usually prevail due to the presence of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  in the combustion gases, and only the most stable chlorides can be prevented from oxidation.

Chlorination in a fused salt bath proves useful when the metal chloride is highly hygroscopic and cannot possibly be introduced into an electrolytic cell without considerable contamination due to water. *In situ* chlorination of a dry oxide in the electrolytic cell renders the feed water-free

and avoids undue loss of metal by bubbling chlorine into the molten salt. Chlorination in a fused salt bath is suspended.

#### DIRECT AND INDIRECT CHLORINATION

There are two main types of chlorination: reduction chlorination and direct chlorination.

The former is used for the chlorination of metals whether or not they are in the form of oxides.

MO (c)

should be negative. It can proceed in the presence of a reducing agent.

Reaction (4.40),

MO (c)

Using the above reaction, all the commercial processes are based on the reduction of chlorides.

We now consider the reduction of chlorides by various reducing agents. The reaction is

MO (c)

MO (c)

The sign of the reaction is negative. Consequently, the reaction is not feasible between the two chlorides.

The direct chlorination is not feasible unless the chlorides are formed.

In general, the reaction is not feasible at very low temperatures. It is not feasible at high temperatures because the reaction is not feasible at high temperatures. This contamination is not feasible at high temperatures.

Where direct chlorination is not feasible, the reduction of chlorides by various reducing agents such as  $\text{S}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_3$ ,  $\text{H}_2\text{O}_4$ ,  $\text{H}_2\text{O}_5$ ,  $\text{H}_2\text{O}_6$ ,  $\text{H}_2\text{O}_7$ ,  $\text{H}_2\text{O}_8$ ,  $\text{H}_2\text{O}_9$ ,  $\text{H}_2\text{O}_10$ ,  $\text{H}_2\text{O}_11$ ,  $\text{H}_2\text{O}_12$ ,  $\text{H}_2\text{O}_13$ ,  $\text{H}_2\text{O}_14$ ,  $\text{H}_2\text{O}_15$ ,  $\text{H}_2\text{O}_16$ ,  $\text{H}_2\text{O}_17$ ,  $\text{H}_2\text{O}_18$ ,  $\text{H}_2\text{O}_19$ ,  $\text{H}_2\text{O}_20$ ,  $\text{H}_2\text{O}_21$ ,  $\text{H}_2\text{O}_22$ ,  $\text{H}_2\text{O}_23$ ,  $\text{H}_2\text{O}_24$ ,  $\text{H}_2\text{O}_25$ ,  $\text{H}_2\text{O}_26$ ,  $\text{H}_2\text{O}_27$ ,  $\text{H}_2\text{O}_28$ ,  $\text{H}_2\text{O}_29$ ,  $\text{H}_2\text{O}_30$ ,  $\text{H}_2\text{O}_31$ 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and avoids undesirable current losses. In some electrolytic processes, a metal chloride is produced by bubbling chlorine through a fused salt bath in which pellets of oxide or carbonate along with carbon are suspended.

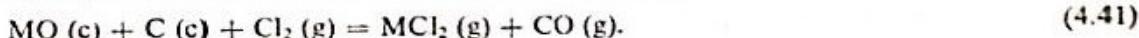
### DIRECT AND INDIRECT CHLORINATION

There are two chief types of chlorination reactions, namely, direct chlorination and indirect or reduction chlorination. Direct chlorination is brought about by chlorine alone whereas reduction chlorination involves some reducing agents as well.

The formation of a metal chloride, usually from an oxide, in the range 700–1000°C, depends on whether or not the metal has a greater affinity for chlorine than for oxygen under the prevailing experimental conditions. In other words, the free energy change for the reaction

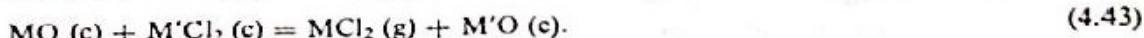


should be negative. If this condition is not fulfilled, then, reaction (4.40) must be aided (so that it can proceed in the forward direction) either by continuously removing the reaction products or by using a reducing agent such as carbon, which would lower the chemical potential of oxygen. Reaction (4.40), for the second situation, may be rewritten as



Using the available free energy data in the literature, we can show that the chlorination of all the commercially important metal oxides proceeds almost to completion under normal industrial operating conditions where, in most cases, the temperature is between 500°C and 1000°C.

We now consider the use of hydrogen chloride and other metal chlorides as chlorinating agents. The reactions are



The sign and magnitude of the free energy changes of reactions (4.42) and (4.43) and, consequently, the extent of chlorination at equilibrium, are largely determined by the differences between the standard free energies of formation of the oxide/chloride pairs.

The direct chlorination of stable oxides such as  $MgO$ ,  $Cr_2O_3$ , and  $Al_2O_3$  is not thermodynamically feasible unless reduced pressures are continuously used to remove the chloride vapours as they are formed at high temperatures.

In general, a sulphide can be directly chlorinated more easily than an oxide as the former reacts at very low temperatures. The vapours generated, however, generally contain  $S_2Cl_2$ , which may itself condense during the condensation of the metal chloride vapours and contaminate the product. This contamination can be avoided if the metal chloride is in the condensed state.

Where direct chlorination is not thermodynamically feasible under 1 atm, for example, in the case of very stable oxides such as  $TiO_2$  and  $ZrO_2$ , reduction chlorination is resorted to. In reduction chlorination, carbon is the most effective reducing agent, although other reducing agents such as  $S$ ,  $CO$ , and  $H_2$  have been tried out.

Free silica by itself is not chlorinated at a temperature below 1000°C in the presence of carbon, whereas silicates such as clay and zircon, when mixed with carbon, are readily chlorinated.

Reduction chlorination can also be carried out using higher valency chloride compounds as reducing agents. For instance, compounds such as  $FeCl_3$ ,  $CrCl_3$ ,  $CuCl_2$ ,  $VCl_4$ ,  $TaCl_5$ ,  $TiCl_4$ , and

$\text{NbCl}_3$  can be used in association with reducing agents such as  $\text{H}_2\text{S}$ ,  $\text{CO}$  and those metals which reduce these compounds to lower chlorides and release the chlorine necessary for chlorination.

A metallic sulphide can be converted to a chloride by treating it with chlorine or  $\text{HCl}$  gas in a neutral or reducing atmosphere. The presence of a reducing agent normally enhances the chlorination rate. Many sulphide ores may be amenable to selective chlorination.

### BENEFICIATION OF LOW-GRADE ORES BY HALOGENATION

The treatment of low-grade ores by chlorination aims at either the removal of undesirable constituents in the form of volatile chlorides by selective chlorination or the recovery of the metallic values also in the form of volatile chlorides. The upgrading of minerals such as ilmenite and chromite is brought about by the selective chlorination and volatilization of the iron oxide impurity. Beneficiation by chlorination is necessary because, in these minerals, iron is present in chemical combination with the desired metals and cannot be eliminated by the conventional ore dressing methods.

During chlorination and the subsequent elimination of iron oxide, the aim is to produce only  $\text{FeCl}_3$ , which has a low boiling point ( $319^\circ\text{C}$ ). Chlorination may also produce the less volatile  $\text{FeCl}_2$  (boiling point  $1026^\circ\text{C}$ ), which tends to choke up the chlorinator. Chlorination carried out with a slight excess of chlorine markedly decreases the production of  $\text{FeCl}_2$ . For example, during the chlorination of ilmenite by  $\text{HCl}$  gas, the formation of  $\text{FeCl}_2$  may be drastically reduced, i.e., from 74 per cent to 1.5 per cent by introducing along with the  $\text{HCl}$  gas a small amount of air (2.8 per cent).

Numerous studies on the selective chlorination of ilmenite have been conducted. These refer to direct chlorination, reduction chlorination using  $\text{C}$ ,  $\text{CO}$ , and  $\text{H}_2$  as reducing agents, and the use of  $\text{CCl}_4$  and  $\text{HCl}$  also as reducing agents. Several studies have also been conducted on upgrading chromite by the selective chlorination of iron oxides in chromite.

Selective or differential chlorination is used for recovering commercially useful metals from low-grade ores such as those of tin, manganese, iron, vanadium, nickel, and tungsten. Differential chlorination is successfully employed for recovering, from monazite, rare-earth metals, thorium, and phosphorus.

Manganese has also been recovered from low-grade ores and slags through chlorination. Chlorination in this case yields chloride vapours which contain both manganese and iron. Additional processing is, therefore, necessary for the elimination of iron. This can be achieved by the selective condensation of the chloride vapours based on the wide difference in the boiling points of  $\text{MnCl}_2$  and  $\text{FeCl}_3$  which are  $190^\circ$  and  $319^\circ\text{C}$ , respectively.

### REFINING OF METALS BY CHLORINATION

Although Chapter 5 describes in detail various methods of refining nonferrous metals, a brief reference, at this stage, to the role of halides in a refining operation is considered appropriate.

Selective chlorination can be effectively used for refining many crude metals. For example, the Betterton process for refining lead, which uses either chlorine or  $\text{PbCl}_2$ , is based on the preferential chlorination of the main impurity zinc at about  $350$ – $400^\circ\text{C}$ . The Goldschmidt process for deleading tin, which uses fused  $\text{SnCl}_2$ , employs selective chlorination of lead in  $\text{Pb}$ – $\text{Sn}$  alloys at around  $250$ – $260^\circ\text{C}$ .  $\text{SnCl}_2$  is reduced to tin by lead which forms a more stable chloride. Any excess  $\text{SnCl}_2$  may be subsequently recovered as volatile  $\text{SnCl}_4$  by chlorination.

Gold bullion can also be refined by chlorination. During chlorination, gold remains unaffected.

while silver, lead, copper, antimony and other impurities are easily chlorinated and removed. Further, Mg can be removed from Al using  $\text{AlCl}_3$ , Zr from a Fe-Zr alloy using  $\text{FeCl}_2$ , Cu from a Cu-Ni alloy using  $\text{NiCl}_2$ , Fe from a Fe-Ni alloy using  $\text{NiCl}_2$ , Fe from a Fe-Ca alloy using  $\text{CaCl}_2$ , Pb from a Pb-Cu alloy using  $\text{CuCl}$ , and Zn from a Zn-Cu alloy also using  $\text{CuCl}$ .

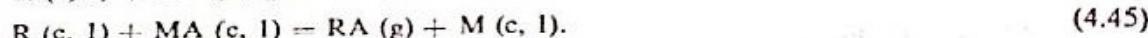
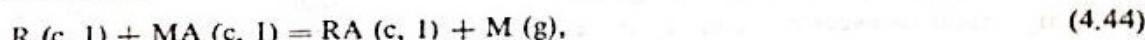
There are also numerous methods in which an intermediate halide vapour is used in metal refining. These methods, often called *vapour transport refining processes*, are discussed in Chapter 5. In Chapter 8, the metathermochemical reduction of halides and the fused salt electrolysis of halide baths are discussed in detail.

#### 4.12 PYROMETALLURGICAL PROCESSES USING VACUUM

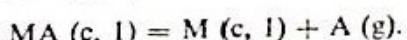
Vacuum techniques found large-scale commercial application in the metallurgical field during the First World War, i.e., when the Germans applied vacuum for degassing steel and purifying certain metals and alloys. Presently, vacuum is widely employed in an increasingly large number of operations used in the extraction and refining of metals. The newer metals such as Ti, Ge, Ta, Nb, and Zr have imparted a new impetus to vacuum processing because they possess, at elevated temperatures, a high affinity for hydrogen and nitrogen. Vacuum has also found application in various other processes such as the distillation of metals and alloys, melting and casting, various heat treatment processes, sintering of metal powders, the deposition of a metal from its vapour state, and joining of metals by brazing and welding. Here, although the emphasis is on the use of vacuum in metal extraction, a brief discussion on some other uses of vacuum is also included to bring out the similarities among the basic principles.

Reactions that are favoured by the application of vacuum can be classified as follows.

##### Thermal Reduction



##### Thermal Dissociation



In reactions (4.44)–(4.46), R is a reducing agent and A is an acid radical, e.g., sulphur, oxygen.

##### Sublimation or Distillation



The equilibrium of each of the reactions (4.44)–(4.48) can be shifted by manipulating the pressure parameter. The use of vacuum helps in eliminating that reaction product which is volatile, thus driving the reaction towards completion. The pressure plays a decisive role in that it changes the free energy-temperature relationships.

The thermal decomposition of oxides under vacuum does not offer any possibilities for metal extraction. This is because most oxides require a very high degree of vacuum and high temperatures. However, relatively unstable oxides such as those of mercury and silver could be decomposed

by applying a vacuum. In both these cases, the metal would have a high vapour pressure at the temperatures required for decomposition, and, consequently, the problem of back reaction arises. Despite these difficulties, vacuum proves useful in the metallocermic reduction of oxides.

In recent years, both the vacuum dissociation and the reduction of sulphides have been investigated. It has been experimentally shown that zinc sulphide can be directly reduced by iron at  $1000^{\circ}\text{C}$  under a vacuum of about 1 mm mercury. This reduction offers interesting possibilities because the roasting and reduction stages are avoided, the metal being produced in a single stage. It is also possible that vacuum influences the metallocermic reduction, by iron, of some other sulphides such as  $\text{PbS}$  and  $\text{HgS}$ .

Apart from sulphides, vacuum can be used also for the dissociation and reduction of halides, hydrides, and nitrides. However, such processes have not yet found application in industry.

When vacuum is applied, distillation and sublimation take place at lower temperatures. As a result, vacuum has found application in titanium and zirconium metallurgy where the crude metal sponge is separated from residual magnesium and magnesium chloride by vacuum distillation.

We now discuss some actual processes where vacuum can play a useful role.

#### REDUCTION OF OXIDE BY CARBON

In the reduction of an oxide by carbon, the volatile reaction products  $\text{CO}$  and  $\text{CO}_2$  lead to an increase in the number of gaseous molecules in the metal-carbon system, and the forward reaction is favoured by lowering the pressure. For example, consider, at  $1200\text{ K}$ , the reaction



In reaction (4.49), the positive free energy change  $\Delta G^{\circ}$  indicates that the forward reaction is not favourable when the reactants and products are in the standard state, i.e., at 1 atm. The necessary degree of vacuum required can be calculated by the procedure now given. We know

$$\Delta G^{\circ} = -RT \ln K,$$

$$68.85 \times 10^3 = -4.575 \times 1200 \log \frac{p_{\text{CO}}^5 \cdot a_{\text{Nb}}^2}{a_{\text{Nb}_2\text{O}_5} \cdot a_{\text{C}}^5}.$$

Here,  $a$  is the activity and  $p_{\text{CO}}$  the partial pressure of  $\text{CO}$ . Assuming the activities of  $\text{Nb}$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{C}$  to be unity,  $p_{\text{CO}}$  is found to be approximately  $3 \times 10^{-3}$  atm or 2.28 mm Hg. Thus, the reaction is made feasible by using a vacuum better than 2.28 mm Hg.

On the other hand, during the reduction of a metal oxide by either hydrogen or carbon monoxide, the number of gaseous molecules in the system remains unchanged. For example, consider the reactions

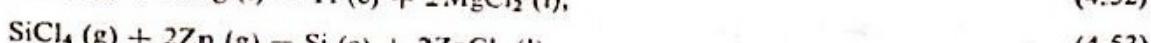
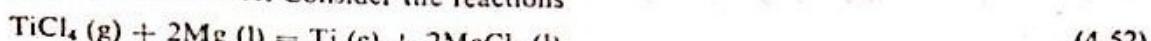


Vacuum would have no effect on the equilibria of these two reactions.

#### METALLOTHERMIC REDUCTION OF OXIDES AND HALIDES

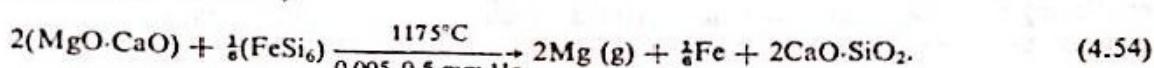
During metallocermic reduction vacuum would aid the reaction *only if there is an increase in the*

number of gaseous molecules. Consider the reactions

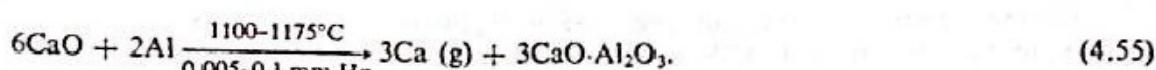


In reactions (4.52) and (4.53), vacuum would obviously have an adverse effect on the equilibrium. However, some metals have been successfully produced by the metallothermic reduction of the metal oxide or the oxygen-bearing compound when the reactants are in a condensed state. We now give examples of such metals.

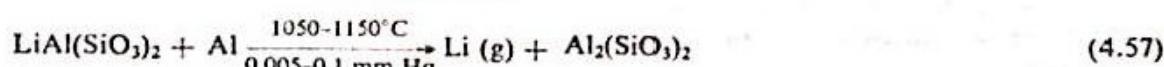
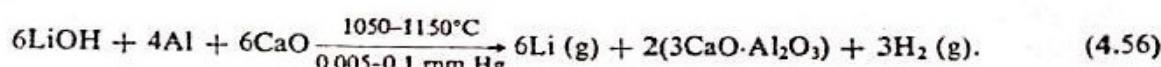
#### Magnesium (Pidgeon Process)



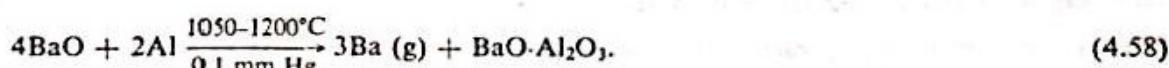
#### Calcium



#### Lithium



#### Barium



Under vacuum, it is also possible to reduce the oxides of Pb, Zn, Mn, and Bi with silicon. However, the conventional methods are much cheaper than reduction under vacuum.

#### DEGASSING OF SOLIDS

Suppose an iron sample is to be degassed so that it contains only 0.0001 wt % hydrogen at 1000°C. It is given that at this temperature the solubility of hydrogen in iron is 0.0005 wt % at 1 atm. According to Sievert's law, hydrogen dissolves atomically and the equation representing the dissolution of hydrogen (with a different standard state for hydrogen as discussed in Section 2.13) is



where H denotes dissolved hydrogen. For reaction (4.59),

$$K = \frac{[\% \text{ H}]^2}{p_{\text{H}_2}}.$$

Since the solubility of hydrogen in iron has been given as 0.0005 wt % at 1 atm, we get

$$K = (0.0005)^2.$$

If  $p'_{H_2}$  is the partial pressure of hydrogen that is in equilibrium with 0.0001 wt % hydrogen in iron, then

$$K = (0.005)^2 = \frac{(0.0001)^2}{p'_{H_2}},$$

$$p'_{H_2} = \left(\frac{0.0001}{0.0005}\right)^2 = \frac{1}{25} \text{ atm} = 30.4 \text{ mm Hg.}$$

Therefore, when the pressure over the iron sample is reduced below 30.4 mm Hg, the hydrogen content can, in principle, be brought below 0.0001 wt %. This pressure can easily be attained by employing a simple vacuum system. In such a situation, the degassing would, however, be slow because the hydrogen has to diffuse through a solid medium.

#### DEGASSING OF LIQUIDS

The required degree of vacuum for degassing of liquid metals and alloys is calculated on the assumption that the gas in equilibrium with the liquid comes from only one source, namely, the liquid in which it has been dissolved. It should be noted that for the solid a uniform pressure throughout the system is assumed. For the liquid, however, the pressure varies along the depth of liquid metal bath because of a metallostatic head. Therefore, the value obtained is valid only if the bath is well-stirred, as would be the case during induction heating. (Stirring would also help speed up the degassing.) If the gas dissolved in the liquid forms compounds such as nitrides, the vacuum must lower the pressure to a value below the decomposition pressure of these compounds.

#### DEOXIDATION OF LIQUID METALS

The deoxidation of liquid metals, in many cases, may be made more efficient by applying a vacuum. For example, consider an iron alloy that contains 0.1 per cent carbon and is melted under a pressure of  $10^{-4}$  atm. If at all deoxidation occurs, it would be according to the reaction



where  $\underline{C}$  and  $\underline{O}$  denote dissolved carbon and oxygen, respectively. For reaction (4.60), the equilibrium constant at  $1600^\circ\text{C}$  is about 420. Assuming the activity coefficients of the dissolved carbon and oxygen to be unity, we get

$$[\% \underline{O}] = \frac{10^{-4}}{420[\% \underline{C}]} = 2.4 \times 10^{-6}.$$

This value of the oxygen content shows that the deoxidation has been very effective.

Vacuum would have no beneficial effect on deoxidation by hydrogen because the number of gaseous molecules would remain unchanged.

#### MELTING

Metals are often melted in an oxide refractory crucible or a furnace lined with an oxide refractory material. The metal-refractory reactions are, therefore, of considerable interest to the process metallurgist. It is, therefore, worthwhile to examine the influence that vacuum can possibly have

on such reactions. Let us consider the reaction



for which the standard free energy change at 1600°C is about +3800 cal. Using the formula,  $\Delta G^\circ = -RT \ln K$ , we get

$$K = \frac{p_{\text{SiO}}^2 \cdot a_{\text{TiO}_2}}{a_{\text{Ti}} \cdot a_{\text{SiO}_2}^2} = 0.36,$$

where  $p$  is the equilibrium partial pressure and  $a$  the activity. Now, when an alloy containing titanium ( $a_{\text{Ti}} = 0.0014$ ) is melted in a refractory crucible whose lining is a silicate containing  $\text{SiO}_2$  ( $a_{\text{SiO}_2} = 0.2$ ), then, using the foregoing equation and assuming the activity of the  $\text{TiO}_2$  formed to be unity, we get

$$p_{\text{SiO}} = (0.36 \times 0.0014 \times 0.04)^{1/2} = 0.0045 \text{ atm or } 3.42 \text{ mm Hg.}$$

Thus, the equilibrium pressure in the system is 3.42 mm Hg. A pressure below this value would result in the constant removal of  $\text{SiO}$  from the system as well as the loss of titanium. Vacuum melting, therefore, cannot ensure oxygen-free metal unless a refractory more stable than  $\text{SiO}_2$  is found. Even if the pressure were normal, reaction (4.61) would continue to proceed if the system were open and  $\text{SiO}$  not allowed to establish an equilibrium pressure, i.e., it is allowed to escape. However, when the same titanium-containing alloy is melted in an alumina crucible, the relevant reaction is



where  $\underline{\text{Ti}}$  denotes titanium in alloy. One of the reaction products, namely,  $\text{Al}$  may form a solution and the standard free energy change for reaction (4.62) at 1600°C is found to be about 35 kcal. Therefore,

$$\Delta G^\circ = -RT \ln K = 35 \text{ kcal.}$$

Hence,

$$K = 8 \times 10^{-5} = \frac{a_{\text{TiO}_2} \cdot a_{\text{Al}}^{4/3}}{a_{\text{Al}_2\text{O}_3}^{2/3} \cdot a_{\text{Ti}}},$$

which gives  $a_{\text{Al}} = (8 \times 10^{-5} \cdot a_{\text{Ti}})^{3/4}$ . We know that the value of  $a_{\text{Ti}}$  is 0.0014, therefore,  $a_{\text{Al}}$  works out to be  $6 \times 10^{-6}$ . This value shows that the contamination due to aluminium is very small, and the application of vacuum to this system cannot bring about the metal-refractory reaction. However, the reaction corresponding to a situation where aluminium is continuously removed by evaporation is



where  $\underline{\text{Al}}$  is aluminium in solution. The equilibrium partial pressure of aluminium over the melt can be estimated. However, this value would be extremely small. A high degree of vacuum would certainly remove aluminium continuously and thus would hinder the attainment of equilibrium, although only marginally. From the foregoing discussion, we conclude that metals can be melted for purification if their reaction with the refractory is avoided.

### 4.13 HYDROMETALLURGY

Hydrometallurgical treatment was generally confined to low-grade ores. However, in recent times, it has been extended to cover concentrates, mattes, splices, and scrap. The stages involved in hydrometallurgical extraction are as follows.

#### PREPARATION OF ORE FOR LEACHING

The preparation of an ore for leaching includes grinding, the physical concentration of the metallic values or the removal of specific impurities by physical methods, roasting, and special chemical treatment either to render these values soluble in the subsequent leaching operation or to prevent the leaching reagent from being consumed by impurities.

#### LEACHING

In leaching, the metallic values in an ore are selectively dissolved using a suitable liquid reagent. The selectivity in dissolution depends on the nature of the reagent while the rate of leaching depends on various factors including temperature, pressure, the volume of the leaching liquid, the ore particle size, the composition and concentration of the reagent, the pulp density, the duration of the leaching reaction, and the degree of aeration of the leaching reagent.

#### SEPARATION OF LEACH LIQUOR

The leach liquor is separated from the residue left behind after processes such as leaching, settling, thickening, filtration, and washing.

#### RECOVERY OF METALLIC VALUES FROM LEACH LIQUOR

The metallic values are recovered from the leach liquor by employing one of the following processes, namely, precipitation, cementation, electrolysis, ion exchange, and solvent extraction.

#### RECYCLING OF LEACH LIQUOR

The leach liquor is recycled after it has been purified and its composition readjusted. A typical hydrometallurgical process could have one or more of the objectives now listed:

- (1) To produce a pure compound which can later be processed by pyrometallurgy to yield the metal.
- (2) To produce the metal from either the crude metal or the metal compound which has already been prepared by other methods.
- (3) To produce a metal directly from an ore or concentrate.

A general outline of the various possible steps for achieving these objectives is shown in Fig. 4.11.

#### ADVANTAGES OF HYDROMETALLURGY

At present, hydrometallurgy is a well-established branch of extraction metallurgy. Complete hydrometallurgical processes are now available for the extraction and refining of almost all metals. In many instances, these processes help in achieving a higher degree of purity and a more economical operation.

The most important advantages of hydrometallurgy are:

- (1) Hydrometallurgical methods are ideally suited for lean and complex ores. With the gradual depletion of rich ore deposits, it is becoming increasingly difficult to apply conventional pyrometallurgical methods for metal extraction.